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ALEXIS EVGRAFOVICH FAVORSKY: A MEMOIR

A. E. Arbuzov

The name of Alexis Evgrafovich Favorsky is connected in my memory with the highlights of my scientific career.

His paternal interest in me began when he participated in awarding me the Zinin and Voskresensky prize for my first major work, "The Structures of Phosphorous Acid and Its Derivatives" (1906). After this event, A. E. Favorsky followed all the steps of my career in science.

I made it a point to drop in on Favorsky every time I came to St. Petersburg. There was no ceremony about these visits, since he treated me like a member of the family. There was always a glass of tea from the samovar, and cake, too. Our conversation ranged over many topics. An ardent sportsman, Favorsky used to enlarge enthusiastically on the subject of hunting. He was the possessor of a magnificent baritone voice and liked to talk about music, too. He informed me there was a period in his life when he vacillated between science and the teaching of singing in choosing his life's work.

During the most important crisis of my career — my battle (with scientific weapons) with the late Professor V. V. Chelintsev — A. E. Favorsky followed every stage of the struggle with keen interest. I recall that when we approached the final stage of that "battle", I asked A. F. Favorsky, as the editor-in-chief of the "Russian Journal of the Physico-Chemical Society" to call a special session of the Society where I, in the presence of his adversaries, would deliver a report on the topic, "The Compounds of Ether with Bromine". My unusual request was granted and an extra meeting was set for January 3, 1913.

I also vividly remember when, on the evening before this debate with V. V. Chelintsev was to take place, I dropped in to see Favorsky. He received me with a stern demeanor and instead of a greeting he said sharply: "Why did you, my dear sir, fall down?" I realized at once that he was referring to an error in the calculation of the calorimetric experiments in my last paper. This was cleared up quickly by Favorsky. It turned out to be nothing dreadful, being merely a matter of multiplying the figures by 3/2. When this was put in order, Favorsky was reassured and our subsequent conversation was calm and friendly.

It is worth mentioning that the debate, for which I prepared myself with great anxiety, never did take place, since my opponent did not appear. The meeting was held just the same, and I delivered the report in the presence of all the prominent chemists of St. Petersburg. On the question of my controversy with V. V. Chelintsev, all the chemists rallied to my side, and on the next morning I was pleasantly surprised when 100 printed copies of the detailed proceedings of the meeting were handed to me.

Another period connected with the personality of A. E. Favorsky is forever impressed on my memory — his participation in the Fifth Mendeleev Congress held in Kazan in 1928, dedicated to the 100th anniversary of the birth of A. M. Butlerov. A. E. Favorsky, as the oldest student of Butlerov, was unanimously elected Chairman of the Congress.

The Fifth Mendeleev Congress, dedicated to the memory of Butlerov, proceeded with great spirit, which also prevailed at the final session, at which Favorsky appealed to the members of the Congress in these inspiring words:

"The work of the Congress is completed. Before adjourning it, I wish to express a feeling which I am sure is shared by all the members of this Congress — the joyous feeling resulting from the consciousness that the army of Russian chemists, consisting chiefly of Butlerovists, continues to uphold the high Butlerov standards.

"We have listened to about 400 reports in pure chemistry and its applications. There was a lively exchange of opinion in the meetings of all sections concerning the reports we heard, a great many of which have unusual interest and value. The fact that the young people came forward with reports in such number is especially encouraging to us, the old members of the Congress. We can pass along to our rising youth the torch of scientific chemical advancement with complete confidence, which justifies our hopes in, and expectations of, the younger chemists. Convening

here in Kazan from all sections of our wide Union, enriched by new valuable and resourceful skills, we find new reserves of energy for further work in every part of the country. It can be said that the Congress proceeded brilliantly. The Soviet Union can rest assured that it is destined for chemization by an adequate core of highly qualified chemists. The desire to express a feeling of deep gratitude to the institutes and to the organizers and authors of the Congress is therefore natural.

"I propose to express appreciation to the Government of the Tatar SSR for its statement of support of the Congress; to Kazan University and its administration as represented by the rector, Prof. A. N. Mishlevsky, and others who not only hospitably opened their rooms for the meetings, but sheltered almost all the members of the Congress; to the Organization Committee of the Congress, with Professor Arbuzov in charge, which spared neither time nor strength in organizing the Congress. I can remember no other Congress at which so much praise and so little criticism can be directed to the organizers.

"The young Kazan chemists also deserve great commendation for their outstanding and gracious service to members of the Congress. We will carry away an excellent impression of them. With a feeling of deep gratitude for our entire experience here, I toast the Tatar Socialist Republic and its Government; I toast the City of Kazan, this Russian Mecca of chemistry; I toast Kazan University, which gave Butlerov to Russian chemists; I toast the members of the Organization Committee and their families, who made themselves responsible for this Congress; and finally, I toast the youth among the Kazan chemists, who are carrying on our glorious past.

"I pronounce the Fifth Mendeleev Congress, dedicated to the memory of A. M. Butlerov, adjourned."

This patriotic and inspiring appeal to the youth brings before my eyes in full stature the powerful figure of Alexis Evgrafovich Favorsky, a most firm believer in the bright future of his native country.

EFFECT OF THE CONCENTRATION OF SOLUTIONS OF ACIDS ON THE HEAT OF THEIR REACTION WITH ZINC AND BARIUM HYDROXIDES

S. A. Shchukarev, L. S. Lilich and V. A. Latysheva

We showed in a work published earlier [1], that the heat of reaction of zinc and cupric hydroxides with two-normal solutions of perchloric and hydrogen halide acids taken in great excess, depends on the nature of the anion of the acid, the heat of reaction becoming less exothermic on passing along the series $HClO_4 > HI > HBr > HCl$.

The observed phenomenon was explained by the reaction of the hydrated ions Zn^{++} or Cu^{++} with halide ions, as a result of which hydrated halide complexes formed. Likewise, it was noted that Yu. Tomsen, investigating objects of the same qualitative composition, did not observe these regularities because of specific conditions of the experiment. He carried out experiments with equivalent quantities of dilute solutions of acids and bases, i. e., at concentration ratios of the components, which were less favorable for the formation of halide complexes than in our investigation, where a considerable excess of the acids was used.

In connection with this, we were interested in the problem of the effect of the concentrations of the acid solutions on the heat of reaction of these solutions with hydroxides. For this, a determination of the heat of reaction of zinc and barium hydroxides with acid solutions of three different concentrations (1, 3 and 4 N) was carried out, in which $Zn(OH)_2$ was reacted with hydrogen halide and perchloric acid solutions, and $Ba(OH)_2$ was reacted only with hydrochloric acid. The investigation of systems of $Ba(OH)_2$ with the remaining above-indicated acids was not necessary, since the absence of the effect of the nature of the anion of the acid on the heat of reaction of $Ba(OH)_2$ with solutions of these acids, even with a large excess of the acid over the theoretical, was established earlier [1]. At the same time, setting up the system, $Ba(OH)_2 - HCl$ solution, for investigation, we expected to show the dependence of the heat of reaction of the hydroxide with the acid solutions on the concentration of these solutions, under conditions of almost complete absence of complex formation and hydrolysis.

EXPERIMENTAL

We used the same semimicro calorimeter for the measurements as in the preceding work [1], with the employment of a thermistor as the heat-measuring apparatus.

The results of the measurements, together with data of the preceding work [1], are presented in Table 1, and in the Figure.

TABLE 1

ΔH of Reaction of Zinc and Barium Hydroxides with Acid Solutions of Different Concentration at 25°

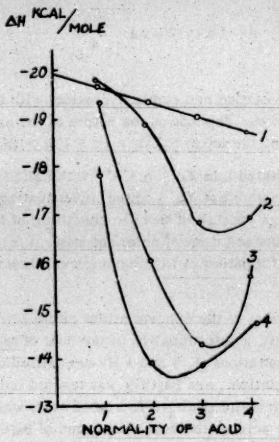
Acid concentration (in N)	Enthalpy change (in kcal/mole of hydroxide)				
	$Zn(OH)_2$				$Ba(OH)_2$
	HCl	HBr	HI	$HClO_4$	HCl
1	−17.78 ± 0.06	−19.27 ± 0.25	−19.72 ± 0.07	−19.66 ± 0.03	−39.59
2	−13.87 ± 0.04	−16.01 ± 0.14	−18.77 ± 0.23	−19.1 ± 0.2	−39.6 ± 0.5
3	−13.78 ± 0.07	−14.40 ± 0.5	−16.73 ± 0.1	−19.08 ± 0.09	−39.64 ± 0.1
4	−14.59 ± 0.12	−15.55 ± 0.01	−16.86 ± 0.03	−18.69 ± 0.06	−40.24 ± 0.23

From the data of Table 1, it is evident that on dissolving $Ba(OH)_2$ in hydrochloric acid, the concentrations of the acid solutions were practically not reflected by the enthalpy change (ΔH). This fact was only a confirmation of the insignificance of the tendency of Ba^{++} ions toward complex formation and hydrolysis.

The observed phenomenon was also confirmed by the idea that the difference in the enthalpy change values in the processes studied, which naturally may appear (even in the absence of processes of complex formation or

hydrolysis) only as a consequence of the non-uniformity of the concentrations of the acid solutions, lies within the limits of experimental error. Such, for example, is the difference in the heats of dilution of the solutions due to the water which formed during the reaction, and subsequently the non-uniform degree of hydration of the cations, etc. This aspect of the problem may therefore be disregarded also in a discussion of the results of experiments with $Zn(OH)_2$.

Unlike $Ba(OH)_2$, for the reaction of $Zn(OH)_2$ with acids, the acid concentration has a strong effect on ΔH.



Change of ΔH in relation to acid concentrations. A) ΔH kcal/mole; B) normality of acids. 1) $HClO_4$; 2) HI; 3) HBr; 4) HCl.

Thus, from the figure it is evident that with an increase of the hydrogen halide acid concentration from 1 to 4 N, ΔH passes through an exothermicity minimum, and for $HClO_4$ a quite appreciable continuous decrease of ΔH with the concentration occurs.

The unusual relationship of the heat of reaction of $Zn(OH)_2$ with $HClO_4$ solutions to the concentration of the latter may be explained hypothetically by the specific reaction of zinc ions with water. Unlike Ba^{++} ions, zinc ions, about which a series of works [2-4] attests, react vigorously with water, which leads to the formation of aquoacids and to a change of the water molecules, down to a splitting off of hydrogen ions. But a reaction of such type must naturally depend on the hydrogen ion concentration in solution; consequently it must depend on the acid concentration.

Another explanation of the dependence of ΔH on the $HClO_4$ concentration, which results from an assumption of the possibility of the formation of a $ZnClO_4^+$ complex, is less probable, since even for cadmium, a much stronger complex former than zinc, the formation of an analogous perchlorate complex occurs, according to Leden's data [5], in a scarcely perceptible quantity, so that it is necessary to suppose that for zinc this effect proves to be within the limits of experimental error.

The minimum on the heat effects – hydrogen halide acid concentration curves is obviously connected chiefly with reaction processes of zinc ions with halide ions, which lead to the formation of complexes. The shape of the curve is apparently determined by the ratio of the quantities of the complexes of different composition which form in the solution and which differ from each other in the magnitude of the heat of formation.

With an increase of the anion concentration, not only an increase of the number of resulting complex ions simplest in composition may occur, but the formation of new more abundant addends of the complexes may occur. Then the presence of an exothermicity minimum on the HCl, HBr and HI curves (see figure) indicates that the formation of zinc-halide complexes in the solutions with high concentrations of addends is accompanied, compared with dilute solutions, by a less endothermic or even an exothermic heat effect.

As is evident from the figure, the minimum appears less deep in the iodide system. This may be explained either by the smaller, compared with Cl^- and Br^-, tendency of I^- ions to form complexes with Zn^{++}, or by the fact that the iodide complexes are on the average less endothermic (in the sense of an enthalpy change) than are the chloride and bromide complexes.

We used the results of the present and preceding works for the calculation of the heat of hydration of the Ba^{++} and Zn^{++} ions. At the same time this was to a certain extent a check on our results and reasoning, since in the literature there were data relative to the heats of hydration of the ions named.

The following formula was used for the calculation:

$$-\Delta H = -U_0 + h_{M^{++}} + 2h_{OH^-} - U_K - 2H + L + X, \qquad (1)$$

where $-\Delta H$ is the heat of reaction of the hydroxide with a solution of the acid; U_0 is the lattice energy of the hydroxide; $h_{M^{++}}$ and h_{OH^-} are the energies of hydration of the metallic and hydroxyl ions, respectively; U_K is the

energy of dissociation of the acid into ions in aqueous solutions; −H is the heat of formation of water from the ions; L is the heat of dilution due to the water which formed again; and X is the heat of reaction of the hydrated cations with the hydrated anions.

In view of the fact that we used strong, highly dissociated acids, and in large excess in relation to the theoretical, it can be assumed that the value of U_K is practically not reflected in the overall heat effect.

Because of the quantity of water which forms on neutralization is negligibly small, compared to the total quantity of water [on the average, as we saw, 1:1700 in systems with $Zn(OH)_2$ and 1:4000 for $Ba(OH)_2$], the value of L also did not exceed the limits of the magnitude of the experimental error.

Finally, proceeding from the above-cited hypotheses relative to the different tendencies of ions toward complex formation with each other, it should be assumed that in the systems $Ba(OH)_2$ − HCl solutions, and $Zn(OH)_2$ − $HClO_4$ solutions, the value of X is also close to zero.

In such a case Equation (1) assumes the form:

$$-\Delta H = -U_0 + h_{M^{++}} + 2h_{OH^-} - 2H \qquad (2)$$

or relative to $h_{M^{++}}$:

$$h_{M^{++}} = -\Delta H + U_0 - 2h_{OH^-} + 2H. \qquad (2a)$$

Substituting into the equation the numerical values of the quantities in the right-hand side, the value of $h_{M^{++}}$ can be determined. These values are as follows: H = − 13.7 kcal [6], and $h_{OH^-} = -115.7$ kcal [7]. The values of U_0 may be calculated from the formula:

$$U_0 = -\Delta H^0_{M(OH)_2} + \Delta H^0_{M^{++}} + 2\Delta H^0_{OH^-}, \qquad (3)$$

where $-\Delta H^0_{M(OH)_2}$ is the heat of formation of the crystalline $M(OH)_2$, $-\Delta H^0_{M^{++}}$ is the heat of formation of the gaseous cation, and $-\Delta H^0_{OH^-}$ is the heat of formation of the gaseous OH^-, equal to +40.5 kcal [7].

Substituting into Equation (2a) the expression for U_0 and the numerical values of H and h_{OH^-}, we obtain the complete formula for the calculation of $h_{M^{++}}$:

$$h_{M^{++}} = -\Delta H - \Delta H^0_{M(OH)_2} + \Delta H^0_{M^{++}} - 339.8 \text{ kcal}. \qquad (4)$$

For barium $\Delta H^0_{M(OH)_2} = -226.2$ kcal [8], and $\Delta H^0_{M^{++}} = -387.7$ kcal [8].

For ΔH we used the value −39.3 kcal, the average of the values found for the 2 N-acids [1]. Substituting all these values into Equation (4), we obtained the heat of hydration value of barium ion, equal to $h_{Ba^{++}}$ 313 kcal.

For zinc $\Delta H^0_{M(OH)_2} = -153.5$ kcal [8], and $\Delta H^0_{M^{++}} = 664.902$ kcal [8], and for ΔH we assumed the value of −19.94, obtained by extrapolation of the heat of reaction curve of $Zn(OH)_2$ with $HClO_4$ solutions of different concentrations to the zero value of the $HClO_4$ concentration, in order to diminish the influence of the excess hydrogen ions in the solution on the heat of reaction.

As a result, the value $h_{Zn^{++}} = 499$ kcal was obtained.

In Table 2 are cited values of the heats of hydration of zinc and barium ions, which we obtained, and also the literature values [7, 9, 10]. A comparison of the values showed their agreement.

TABLE 2

Heats of Hydration of Zn^{++} and Ba^{++} Ions

$h_{Zn^{++}}$	$h_{Ba^{++}}$	Literature sources
501	312	[9, 10]
492	313	[7]
499	313	Our data

SUMMARY

1. The heat of reaction of crystalline barium hydroxide with hydrochloric acid solutions, taken in great excess over the theoretical, under the conditions which we investigated, had practically no dependence upon the acid concentration.

2. An increase of perchloric acid solution concentrations from 1 to 4 N led to a gradual decrease of the exothermicity of the heat of reaction of $Zn(OH)_2$ with $HClO_4$ solutions.

3. The heat of reaction of $Zn(OH)_2$ with HCl, HBr and HI solutions, with an increase of the concentration of the acid solutions from 1 to 4 N, passed through an exothermicity minimum, which was accounted for by the appearance in solution of the less endothermic or exothermic zinc halide complexes.

4. On the basis of the work done, the calculated values of the heats of hydration $h_{M^{++}}$ of the Ba^{++} and Zn^{++} ions, equalled 313 and 499 kcal, respectively.

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DIENES OBTAINED BY DEHYDRATION OF 3,4-DIMETHYLHEXANEDIOL-3,4 (PINACOL OF METHYL ETHYL KETONE)

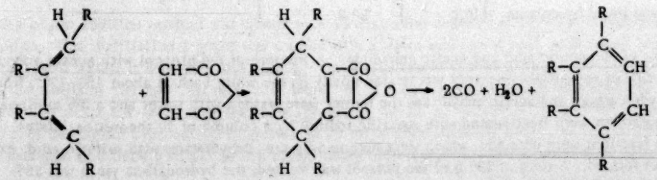
I. V. Gostunskaya, E. A. Krasnyanskaya and B. A. Kazansky

MacCalum and Whitby [1] studied the dehydration of 3,4-dimethylhexanediol-3,4. They distilled pinacol with drops of dilute sulfuric acid and obtained an 84% yield of dehydration product. In 1940 Schmerling, Friedman and Ipatieff [2] subjected 3,4-dimethylhexanediol-3,4 to simultaneous dehydration and hydrogenation in the presence of nickel, applied to aluminum oxide, and at once obtained saturated 3,4-dimethylhexane. In 1946 Takeshi Kuwata [3] dehydrated 3,4-dimethylhexanediol-3,4 in the presence of sulfuric acid or alumina, and observed that in both cases pinacoline, together with the unsaturated hydrocarbons, formed.

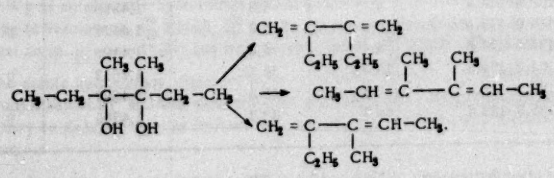
Of the investigators named, only MacCalum and Whitby studied the hydrocarbon portion of the 3,4-dimethylhexanediol-3,4 dehydration product and concluded that one hydrocarbon, namely, 3,4-dimethylhexadiene-2,4, was obtained in this reaction.

At 0°, MacCalum and Whitby's diene added 2 bromine atoms, and at room temperature, 4; it had no greater capacity for thermopolymerization than did isoprene and dimethylbutadiene; sulfuric acid converted it to the dimer.

Interested in the order of the addition of hydrogen to dienes of different structure, and wishing to subject to this reaction a hydrocarbon for which the methyl groups would be connected with all four carbons of a conjugated system, we carried out the dehydration of 3,4-dimethylhexanediol-3,4, both according to MacCalum and Whitby [1] and according to Lebedev [4], i. e., in the presence of acetic anhydride and phosphoric acid. On distillation of the dehydration products, which resulted in both cases, by a column of 70 theoretical plates, 3 diene hydrocarbons, and not 1 as indicated by Maccalum and Whitby, were isolated. For determination of their structure, their addition compounds with maleic anhydride were synthesized, which were then converted to aromatic hydrocarbons by distillation with phosphoric anhydride, according to Levina and Skvarchenko [5]:



Since at this time 1,2,3,4-tetramethylbenzene (prenitol), 1,2-diethylbenzene and 1,2-dimethyl-3-ethylbenzene were formed from the dienes obtained, we may conclude that the corresponding dienes have the structure of 3,4-dimethylhexadiene-2,4; 2,3-diethylbutadiene-1,3; and 3-methyl-2-ethylpentadiene-1,3, i. e., that the dehydration reaction of 3,4-dimethylhexanediol-3,4 went not only according to MacCalum and Whitby's scheme, but also according to the two other possible directions:



EXPERIMENTAL

1. Synthesis of 3,4-dimethylhexanediol-3,4. The initial methyl ethyl ketone had a b. p. of 79.6° (760 mm), n_D^{20} 1.3795, d_4^{20} 0.8040. 0.7 mole of the ketone and 0.07 mole of mercuric chloric were dissolved in 160 ml of benzene (Mixture I); 1.4 moles of the ketone was mixed with 80 ml of benzene (Mixture II). Mixture I was added gradually to 1.0 mole of Mg; the reaction began at once or after slight heating. After addition of Mixture I, Mixture II was added [6]; after spontaneous boiling for 1 hour, 120 ml of benzene was added, and the flask was heated for 2 hours on the water bath. The resulting magnesium derivative of the pinacol was decomposed with hot water, the magnesium hydroxide precipitate was separated and extracted with fresh benzene. The benzene solutions were combined, separated from water, dried by solid sodium hydroxide, the benzene was removed, and the pinacol was vacuum distilled. The 98-106° (6 mm) fraction obtained with a yield of 30-32%, contained chiefly 3,4-dimethylhexanediol-3,4, which on standing formed as crystals with a m. p. of 46-47°. On distillation by a column with glass caps to a height of 60 cm, the pinacol boiled at 119° (25 mm). The non-crystallizing portion, as N. D. Zelinsky indicated [7] was apparently its stereoisomer.

2. Dehydration of the pinacol. a) In the presence of sulfuric acid. 0.36 mole of the pinacol and 3 drops of 20% H_2SO_4 were heated gradually on the oil bath at about 180°, with removal of the mixture of hydrocarbons and water. After salting out of the hydrocarbon layer with potash and drying, it was distilled by a column of 70 theoretical plates in a quantity of 34 ml.

The results of the distillation and the characteristics of the resulting fractions are cited in Table 1.

TABLE 1

Fractions	Boiling point at 760 mm	Quantity		n_D^{20}	d_4^{20}
		(in ml)	(in vol. %)		
1	111.3-125.1°	3.7	8.6	1.4454	–
2	125.1-125.5	6.8	15.8	1.4616	0.7762
3	125.5-134.7	3.3	7.7	1.4682	–
4	134.7-136.2	12.3	28.6	1.4761	0.7914
5	136.2-150.7	3.8	8.8	1.4555	–
6	150.7-152.7	3.1	7.2	1.4381	–
Residue in flask and losses by column		10.0	23.3		

b) In the presence of phosphoric acid and acetic anhydride. A mixture of the pinacol with acetic anhydride (1:4) and several crystals of orthophosphoric acid was heated slowly on the water bath at about 160-170°; from the distilled mixture of hydrocarbons and acetic anhydride, the former were washed with water and a 3% solution of soda. The dried hydrocarbons were fractionated with metallic sodium by a column of 70 theoretical plates. Approximately the same fractions were obtained which were obtained by the dehydration with sulfuric acid, except that pinacoline was not formed. A total of 230 g of the pinacol was treated; the hydrocarbon yield was 86%. The results of their distillation are cited in Table 2

TABLE 2

Fractions	Boiling point at 760 mm	Quantity		n_D^{20}	d_4^{20}
		(in ml)	(in vol. %)		
1	108.8-114.0°	6.5	6.3	1.4390	–
2	114.0-115.6	8.0	7.8	1.4428	0.7591
3	115.6-124.8	4.4	4.3	1.4490	–
4	124.8-126.3	10.4	10.1	1.4613	0.7768
5	126.3-135.8	17.6	17.0	1.4690	–
6	135.8-136.3	48.7	47.0	1.4760	0.7919
Residue in flask and losses by column		7.4	7.2		

After repeated precise fractionation of all the resulting products by the same column, 3 hydrocarbons with the following properties were separated:

I. B. p. 114.4-114.8° (760 mm), n_D^{20} 1.4410, d_4^{20} 0.7540, MR_D 38.52; Calc. for $C_8H_{14}F_2$ 38.21, EM_D 0.31.

Found %: C 87.19, 87.21; H 12.85, 12.89. C_8H_{14}. Calculated %: 87.19; H 12.81.

II. B. p. 126.3° (760 mm), n_D^{20} 1.4610, d_4^{20} 0.7760, MR_D 38.89; calc. for $C_8H_{14}F_2$ 38.21, EM_D 0.68.

Found %: C 87.06, 87.10; H 12.68, 12.81. C_8H_{14}. Calculated %: C 87.19; H 12.81.

III. B. p. 136.3° (760 mm), n_D^{20} 1.4760, d_4^{20} 0.7918, MR_D 39.21; calc. for $C_8H_{14}F_2$ 38.21. EM_D 1.00.

Found %: C 86.74, 86.79; H 12.71, 12.83. C_8H_{14}. Calculated %: C 87.19; H 12.81

The hydrocarbon, described by MacCalum and Whitby [1], had a b. p. of 132-134°, n_D^{20} 1.4630, d_4^{20} 0.7786, MR_D 38.78, i. e., it was apparently a mixture of Hydrocarbons II and III.

Their capacity to give addition compounds with maleic anhydride and to add 2 moles of hydrogen in the presence of palladium indicated that Hydrocarbons I, II and III were dienes. They differed rather considerably from each other in their physical properties; this pertained especially to Hydrocarbon I, which merited further study. However, in the literature an instance of a large difference in the constants of the isomeric octadienes was recorded, for example [8]:

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH=\underset{\underset{CH_3}{|}}{C}-CH_3,$$ b. p. 134.5°, d_4^{20} 0.7615, n_D^{20} 1.4781.

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-\underset{\underset{CH_3}{|}}{C}=CH-CH_3,$$ b. p. 114.0-114.2°, d_4^{20} 0.7497, n_D^{20} 1.4429.

3. Investigation of the dehydration products of 3,4-dimethylhexanediol-3,4.

a) Hydrocarbon with b. p. of 114.4-114.8°. (9 g, or 0.082 mole) was introduced into reaction with 8.35 g (0.085 mole) of maleic anhydride dissolved in 10 ml of benzene. The formation of an addition compound proceeded slowly on heating in a sealed ampoule on the oil bath at 115-120° for 9 hours. The vacuum-distilled addition product (b. p. 148-150° at 5 mm) melted at 46-47°. The yield was about 70%.

13 g of the addition product was mixed with an equimolar quantity of phosphoric anhydride and subjected to dry distillation. The distillation product was washed with a warm solution of soda, with water, with 80% sulfuric acid and again with water; it was dried over $CaCl_2$. On distillation of it over metallic sodium, the main volume boiled within the limits of 190-200°; its properties were: m. p. −10°, b. p. (according to Sivolobov) 199-200°, n_D^{20} 1.5188, d_4^{20} 0.9040. For 1,2,3,4-tetramethylbenzene (prenitol) the m. p. was −6.25°, b. p. 205°, n_D^{20} 1.5203, d_4^{20} 0.9046. 0.3676 g of the dienic hydrocarbon (dissolved in 20 ml of ethyl alcohol) at 22° and 744 mm absorbed 164 ml of H_2 in the presence of 0.0886 g of palladium black; under these conditions 164.4 ml of H_2 (2 moles) must be absorbed.

From all that has been stated, it can be deduced that the hydrocarbon was 3,4-dimethylhexadiene-2,4.

b) The hydrocarbon with a b. p. of 126.3°. (17.2 g or 0.156 mole) reacted with maleic anhydride in benzene solution. The formation of an addition compound took place instantaneously with a large evolution of heat. Its yield was about 90%. After vacuum distillation and recrystallization the addition product had a m. p. of 59°.

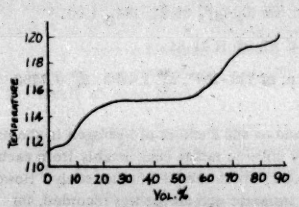
12 g (0.05 mole) of the addition product was subjected to dry distillation with an equivalent quantity of phosphoric anhydride. 4 g of an aromatic hydrocarbon with the following properties was collected: m. p. −31°, b. p. 182-183° (according to Sivolobov), n_D^{20} 1.5048, d_4^{20} 0.8839. In physical properties, the hydrocarbon mostly resembled 1,2-diethylbenzene; its m. p. was −31.44° and its b. p. was 183.5°, n_D^{20} 1.5034, d_4^{20} 0.8805 [9].

0.3695 g of the dienic hydrocarbon, dissolved in 20 ml of ethyl alcohol, added 166 ml of H_2 in the presence of 0.091 g of palladium black at 21° and 744 mm; 165.6 ml was calculated for $2H_2$ under these conditions. From all the data cited, it may be deduced that the hydrocarbon with a b. p. of 126.3° was 2,3-diethylbutadiene-1,3 (3,4-dimethylenehexane).

c) The hydrocarbon with a b. p. of 136.3°. (7.09 g, or 0.072 mole) was reacted with 7.05 g (0.072 mole) of maleic anhydride in 10 ml of benzene. The reaction began immediately with strong frothing and evolution of heat;

a rose color appeared. After removal of the benzene and vacuum distillation of the residue 12 g of the addition product with a m. p. of 104° was obtained. Its yield was about 80%.

10 g of the addition product and an equivalent quantity of P_2O_5 was heated on the burner flame at about 150°, after this the temperature rapidly rose to 190°, and the decomposition products began to distill. The aromatic hydrocarbon separated from them had a m. p. of −46°, a b. p. of 194-195° (according to Sivolobov), n_D^{20} 1.5123, d_4^{20} 0.8945. In these properties it closely resembled 1,2-dimethyl-3-ethylbenzene; its m. p. was −49.5°, its b. p. was 193.8°, n_D^{20} 1.5117, d_4^{20} 0.8920 [9]; therefore, the structure of 3-methyl-2-ethylpentadiene-1,3 could be attributed to the diene with a b. p. of 136.3°



Distillation curve of products of hydrogenation of 3-methyl-2-ethylpentadiene-1,3 over palladium black.

0.3598 g of the diene in 20 ml of ethyl alcohol, in the presence of 0.088 g of palladium black, at 22.5° and 742 mm, added 162 ml of H_2; for $2H_2$ under these conditions 162.8 ml was calculated.

The indicated structure of the diene was confirmed again by the investigation of the products of the addition of 1 mole of H_2 to it. As is readily seen, owing to the asymmetrical structure of the diene, not 2, as for the hydrocarbons with a b. p. of 114.4-114.8° and 126.3°, but 3 monoolefins were obtained at this time: 3-methyl-2-ethylpentene-1 with a b. p. of 112.5° (760 mm), n_D^{20} 1.4142, d_4^{20} 0.7290; 3,4-dimethylhexene-2 with a b. p. of 116° (760 mm), n_D^{20} 1.4180, d_4^{20} 0.7370; and 3,4-dimethylhexene-3 with a b. p. of 122° (760 mm), n_D^{20} 1.4300, d_4^{20} 0.7470 [9].

Actually, on the distillation curve (figure) of the product of the addition of 1 mole of H_2 to the diene with a b. p. of 136.3°, three horizontal areas were obtained, which corresponded to temperatures of 112° (760 mm) (n_D^{20} 1.4180, d_4^{20} 0.7317), 115° (760 mm), (n_D^{20} 1.4210, d_4^{20} 0.7346) and 119° (760 mm) (n_D^{20} 1.4290, d_4^{20} 0.7400). It is necessary to keep in mind that in these fractions there may be small quantities of unreacted diene.

SUMMARY

On dehydration of 3,4-dimethylhexanediol-3,4 in the presence of sulfuric or phosphoric acids, three dienes, and not one, as indicated in the literature, were obtained. Their structure was demonstrated by the decomposition of their addition products with maleic anhydride; they proved to be 3,4-dimethylhexadiene-2,4; 2,3-diethylbutadiene-1,3 and 3-methyl-2-ethylpentadiene-1,3. From what has been stated it follows that the splitting off of two molecules of water from 3,4-dimethylhexanediol-3,4 took place in all of the possible directions. 3-Methyl-2-ethylpentadiene-1,3 formed in the largest quantity.

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SYNTHESIS OF BRANCHED DIACETYLENE HYDROCARBONS

PRODUCTION OF 2,2,5,5,8,8-HEXAMETHYLNONADIYNE-3,6

A. I. Zakharova and G. M. Murashov

In a series of works [1] it was shown that tertiary acetylene chlorides of the propargyl type $R_3CCl-C\equiv C-R$ react readily with organomagnesium compounds of the saturated series with the formation of branched monoacetylene hydrocarbons. By such a method we were recently able to synthesize the first representative of the acetylene hydrocarbons with three quaternary carbon atoms, the completely methylated monoacetylene – 2,2,3,3,6,6-hexamethylheptyne-4 [2].

It was of interest to investigate the feasibility of the application of these chlorides to the synthesis of branched diacetylene hydrocarbons. The present work also had the purpose of proposing a new method of production of the diacetylenes by the reaction of propargyl-type tertiary acetylene chlorides with alkynylmagnesium halides of the $R-C\equiv CMgBr$ type.

The diacetylene hydrocarbons described in the literature, which number beyond sixty representatives, in the main have a straight chain of carbon atoms. Methods of production of the diacetylenes are: 1) dehydrohalogenation of tetrahalide-substituted saturated hydrocarbons [3], dihalide-substituted diolefins [4]; and monohaloid-substituted vinylacetylenes [5]; 2) dehalogenation of tetrahalide-substituted diolefins [6]; 3) oxidation of monoacetylenides in the presence of oxygen [7], potassium ferricyanide [8], the dihalide of copper [9], nitrobenzene [10], iodine [11], etc.; 4) alkylation of monoacetylenides by dihalide derivatives of the saturated series [12] and alkylation of non-substituted and mono-substituted diacetylenes [13]; 5) condensation of propargyl-type halide derivatives [14]; 6) polymerization of acetylene in an electric discharge [15], and 7) the reaction of monoacetylenides with alkynyl halides [14b, 16].

Of the branched diacetylene hydrocarbons with aliphatic radicals, the following which contained quaternary carbon atoms were especially interesting to us: 1) tert.-butyldiacetylene $(CH_3)_3C-C\equiv C-C\equiv CH$, synthesized from trimethylacetaldehyde and the Grignard reagent from propargyl alcohol, followed by conversion to the hydrocarbon via the dichloride [17], and 2) di-tert.-butyldiacetylene $(CH_3)_3C-C\equiv C-C\equiv C-C(CH_3)_3$, obtained by oxidation of tert.-butylacetylenemagnesium bromide in the presence of nitrobenzene [10], and by heating the copper derivative of tert.-butylacetylene, or by its oxidation with potassium ferricyanide [8b].

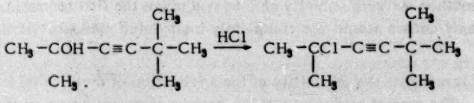
In 1902 the mono- and di-alkyne-1-magnesium dibromides $R-C\equiv C-MgBr$ and $BrMg-C\equiv C-MgBr$ were introduced into practice for the first time by Iotsich [18]. Much later, in 1935, Marvel and coworkers [19] obtained an organomagnesium complex of the $R-C\equiv C-\underset{|}{\overset{|}{C}}-MgBr$ type, but were generally unable to obtain the Iotsich complex from the halide of the $R-C\equiv C-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-X$ type [20].

The use of alkynyl halides of the $R-C\equiv CX$ type as the second component in the reaction with the Iotsich complex was first accomplished by Grignard in 1926 [16a]. Halides of the propargyl type $R-C\equiv C-CH_2X$ were used in reactions with the alkylmagnesium halides for production of di-substituted monoacetylenes [21] and, as far as we know, the same conditions of propargylation of the Iotsich complex of halides of the $R_3CCl-C\equiv C-R$ type were not described in the literature.

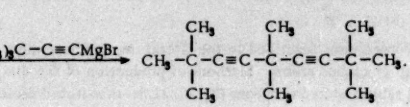
Moreover, it is necessary to note that the application of alkyne-1-magnesium bromides to the synthesis of mono- and di-substituted acetylenes has been worked out in a few instances. Thus, by the reaction of furfuryl bromide [22], allyl chloride and bromide [12a, 23], benzyl bromide [24] and, finally, triphenylchloromethane [25], with different alkyne-1-magnesium halides, the corresponding di-substituted monoacetylenes were obtained. Either we were unable to obtain the same acetylene hydrocarbons by the condensation of alkyne-1-magnesium bromides with saturated alkyl halides under ordinary conditions [26], or the reaction took place with negligible yields [24, 27].

In the literature there are indications that Grignard-Würtz syntheses were carried out in some instances by the use of the halide salts of some metals as catalysts. Mercuric chloride was first used as a catalyst in the synthesis of paraffin hydrocarbons with a quaternary carbon atom [28]; Cu_2I_2 and $HgCl_2$ were used successfully in the synthesis of tetralkylmethanes [29]; Cu_2Cl_2 and $CrCl_3$ were used in the condensation of arylmagnesium bromides with alkyl-vinyl bromides [30]; Cu_2X_2, $Cu_2(CN)_2$ and CuX_2 were used in the reaction of allyl bromide with alkylmagnesium acetylenes [23]; more recently di-substituted acetylenes, vinyl acetylenes and α-diacetylenes [16b] were obtained in the presence of Cu_2Cl_2 and $CoCl_2$.

Keeping in mind all that has been presented above, for the purpose of development of a new method of synthesis of diacetylene hydrocarbons and of production of the first representative of the completely methylated diacetylenes with three quaternary carbon atoms, 2,2,5,5,8,8-hexamethylnonadiyne-3,6 (III), we decided to carry out the condensation of tert.-butylacetylenemagnesium bromide with a tertiary acetylene chloride of the propargyl type, 2,2,5-trimethyl-5-chlorohexyne-3 (II), in the presence of $HgCl_2$ and Cu_2Cl_2. The chloride (II) was obtained [31] by the action of gaseous hydrogen chloride on the carbinol (I) by a method which we developed earlier, and the carbinol (I) was in its turn synthesized by the Favorsky reaction from tert.-butylacetylene and acetone.



(I) (II)



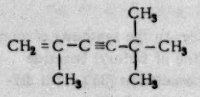
(III)

The experiment completely justified our expectations. As a result of the reaction an 80% yield (by calculation on the chloride used) of a product with a m. p. of 46° was obtained, the elementary analysis and determination of molecular weight of which gave the formula $C_{15}H_{24}$. A spectrographic investigation of the hydrocarbon by the Raman method* showed the presence of a triple bond (2221 cm^{-1}). The hydrocarbon was very stable toward oxidation. It was recovered unaltered after heating at approximately boiling for 3 days with a 1% solution of $KMnO_4$. The structure of Hydrocarbon (III) was demonstrated by ozonization. Trimethylacetic, dimethylmalonic, and hydroxyisobutyric acids were obtained as a result of the decomposition of the ozonolysis products. The presence of the first two acids was entirely regular and demonstrated completely the structure of Hydrocarbon (III). As to hydroxyisobutyric acid, its presence in the ozonization products of Hydrocarbon (III) apparently may be accounted for by the partial decarboxylation of dimethylmalonic acid under the reaction conditions, with subsequent oxidation of the isobutyric acid formed at this time to hydroxyisobutyric acid.

According to Busch [32], four molecules of hydrogen were added by the hydrogenation of Hydrocarbon (III) in the presence of $PdCl_2$ on $CaCO_3$.

Beside Hydrocarbon (III), in the reaction between tert.-butylacetylenemagnesium bromide and chloride (II), a product with a b. p. of 48° at 100 mm was obtained with a yield of about 20% (by calculation on the chloride used).

A determination of the molecular weight and an elementary analysis of this compound gave the formula C_9H_{14}, and an investigation of the Raman spectrum showed the presence of double and triple bonds. This hydrocarbon was apparently a product of the cleavage of HCl from the original chloride (II), and had the structure of 2,5,5-trimethylhexen-1-yne-3 (IV). The constants of the hydrocarbon are given in the Experimental, but its structure was not closely investigated.



(IV)

* For a description of the method of taking the Raman spectrum, see the Experimental Section.

EXPERIMENTAL

Production of dimethyl-tert.-butylacetylenecarbinol (2,2,5-trimethylhexyn-3-ol-5 (I). The alcohol was obtained by A. E. Favorsky's method. 150 g of powdered potassium hydroxide and 200 ml of absolute ether were placed in a three-necked flask, equipped with a rapidly-rotating propeller stirrer, reflux condenser and dropping funnel. With rapid stirring, and with cooling to about 0° provided by ice water, a mixture of 0.5 mole of tert.-butylacetylene and 0.5 mole of acetone in 50 ml of absolute ether was added dropwise during 4 hours. The reaction mixture was left for 12 hours, with stirring, and then, with cooling, it was decomposed with water. The ether layer was removed from the alkaline solution and dried by calcined magnesium sulfate. After removal of the ether, the acetylene alcohol (I) was purified by 2 vacuum distillations. Its yield was 88.6%. The carbinol crystallized on standing.

B. p. 52° at 10 mm, 62° at 17 mm, m. p. 34°, n_D^{35} 1.42448, n_C^{35} 1.42190, n_F^{35} 1.43057, n_G^{35} 1.43991.

The carbinol (I) was described in the literature [1b]. It was obtained by an organomagnesium synthesis, according to Grignard. Its b. p. was 85° at 60 mm, 150° at 743 mm, and its m. p. was 31.8-32°, d^{38} 0.8064, n_D^{38} 1.4222.

Production of dimethyl-tert.-butylacetylenechloromethane (2,2,5-trimethyl-5-chlorohexyne-3) (II). 62 g of the carbinol (I) in portions of 5-10 g each, with cooling, was treated with gaseous hydrogen chloride, by a method which we proposed earlier [32]. The chloride which formed was separated from the water which formed during the reaction, dried with $CaCl_2$ and vacuum distilled. Its yield was 85.5%.

B. p. 72° at 70 mm, n_D^{20} 1.43598, n_C^{20} 1.43322, n_F^{20} 1.44285, n_G^{20} 1.45194.

The chloride was described in the literature [1b]. It was obtained by the action of HCl on the carbinol (I), in ligroin in the presence of solid $CaCl_2$. Its b. p. was 81-81.5° at 100 mm; its m. p. was 15-15.2°, d^{20} 0.8585, n_D^{20} 1.4343.

Production of 2,2,5,5,8,8-hexamethylnonadiyne-3,6 (III) and 2,5,5-trimethylhexen-1-yne-3 (IV). 41 g of tert.-butylacetylene in 50 ml of ether was added during 4 hours, with constant stirring and cooling, to the Grignard reagent prepared by the usual method from 12 g of magnesium and 65 g of ethyl bromide in 200 ml of absolute ether. After standing for 8 hours with cooling, the reaction mixture was heated on the water bath at 30-38° until cessation of the evolution of ethane, and was then cooled to room temperature. A mixture of 1 g of Cu_2Cl_2 and 1 g of $HgCl_2$ was introduced as a catalyst into the tert.-butylacetylenemagnesium bromide complex thus obtained, and 40 g of chloride (II) was added, with cooling. The reaction mixture was left, with stirring, for 3 days, and then was decomposed, with cooling, by dilute hydrochloric acid. The ether solution was dried with calcined magnesium sulfate, and the ether was removed. Two fractions were separated from the reaction products after 3 vacuum distillations: the 1st fraction, according to analysis, was the enyne hydrocarbon (IV), which was not described in the literature.

B. p. 58° at 100 mm, d_4^0 0.7825, d_4^{20} 0.7682, n_D^{20} 1.43851, n_C^{20} 1.43460, n_F^{20} 1.44704, n_G^{20} 1.45697, MR_D 41.80, MR_C 41.48, MR_F 42.51, MR_G 43.32. C_9H_{14} FF. Calculated: MR_D 41.23, MR_C 41.02, MR_F 41.88, MR_G 42.33; ω_{FC} 28.37.

Found %: C 88.63; H 11.68; M 118.6, 120.6. C_9H_{14}. Calculated %: C 88.45; H 11.55. M 122.2.

The Raman spectrum of the hydrocarbon was taken with a triple-glass prism spectrograph with a system of three ISP-51 prisms of constant diffraction (excitation of Hg 22938 cm^{-1} line, a light filter of glass, a slit width of 0.007 mm, and an exposure of 6 hours). The intensity of the lines was evaluated visually on a 10-mark scale.

149.1 (3), 531.6 (1), 560.7 (1), 863.6 (5), 919.0 (2), 1200.1 (3), 1376.0 (1), 1444.4 (5), 1627.0 (10), 2202.9 (10), 2915.9 (1), 2967.3 (1).

An analysis of the 2nd fraction showed that it was the diacetylene hydrocarbon (III).

B. p. 82° at 15 mm, 74° at 5 mm, m. p. 46°, d_4^{50} 0.7482, n_D^{50} 1.41735, n_C^{50} 1.41469, n_F^{50} 1.42356, n_G^{50} 1.43293; MR_D 68.73, MR_C 68.35, MR_F 69.63, MR_G 70.97. $C_{15}H_{24}$ FF. Calculated: MR_D 67.34, MR_C 67.05, MR_F 68.34, MR_G 68.99; ω_{FC} 21.25.

Found %: C 88.21, 88.00; H 11.87, 11.65. M 206.2, 201.0. $C_{15}H_{24}$. Calculated %: C 88.16; H 11.84. M 204.3.

Since Hydrocarbon (III) had a m. p. of 46°, both methods were used for its spectrographic investigation by the Raman method. In order to eliminate the effect of the solvent, and to avoid the necessity of growing a monocrystal, as is usually done, the hydrocarbon was used in the molten state. For this it was placed in a cuvette, equipped with

an electric heater (a nichrome wire coil, l of 1.5 m, d 0.3 mm, which was connected into the electric circuit through a rheostat). For taking of the spectrum the substance was recrystallized three times from methanol or was purified by vacuum sublimation. On recrystallization, the substance was not filtered through a paper filter, since the tiniest fragments of paper fiber greatly hindered the taking of the spectrum, but was filtered hot through a Schott filter in a thermostat.

The Raman spectrum of the hydrocarbon (III):* 139.0 (2), 166.4 (2), 445.5 (0.5), 547.5 (1), 608.9 (1), 741.6 (0.5), 886.5 (3), 919.5 (2), 1190.8 (1), 1195.8 (4), 2220.8 (5).

Ozonization of Hydrocarbon (III). 10 g of the hydrocarbon was ozonized in a solution of 100 ml of purified chloroform until cessation of the absorption of ozone. The solvent was removed in vacuo; the ozonide was decomposed with water, at first at ordinary temperature, then on heating on the water bath. The solution of the ozonization products had an acid reaction. It was neutralized by powdered chalk. On steam-distillation of the neutral ozonolysis products a small quantity of a yellow-green oil came over, the nature of which was not closely investigated. The solution which remained after removal of the neutral products was acidified with sulfuric acid. On removal of the volatile acids from the acid products, several fractions of about 10 ml each were collected, which on heating with freshly-prepared silver carbonate formed the silver salts corresponding in composition to trimethylacetic acid.

Found %: Ag 51.63, 51.69, 51.42. $C_5H_9O_2Ag$. Calculated %: Ag 51.62.

Besides the liquid fractions, on removal of the volatile acids, 0.3 g of a crystalline acid with a m. p. of 78° was collected. A test of a mixture with hydroxyisobutyric acid showed no melting point depression. An ether extraction was made from the residue after removal of the volatile acids. After drying and removal of the ether, crystals with a m. p. of 188° were obtained.** A test of a mixture with dimethylmalonic acid gave no melting point depression.

A weighed portion of dimethylmalonic acid was neutralized by the calculated quantity of a titrated solution of KOH, and then the silver salt of the acid was precipitated by a 10% solution of $AgNO_3$.

Found %: Ag 62.19, 62.09. $C_5H_6O_4Ag_2$. Calculated %: Ag 62.38.

Hydrogenation of Hydrocarbon (III). 2 g of a catalyst, prepared according to Busch [32] ($PdCl_2$ on $CaCO_3$), in 50 ml of ethyl alcohol, was saturated with hydrogen, and then 1 g of Hydrocarbon (III) was introduced. The addition of hydrogen in the first 10 minutes went very energetically and 420 ml was absorbed; then the absorption proceeded at a decreasing rate, and in 8 hours 440 ml more of hydrogen was added, making a total of 860 ml. Theoretically, 876 ml of H_2 is required for the saturation of two triple bonds.

SUMMARY

1. A new method of production of branched diacetylene hydrocarbons by propargylation of the alkyne-1-magnesium bromides by tertiary acetylene chlorides of the $R_2CCl-C\equiv C-R$ type in the presence of $HgCl_2$ and Cu_2Cl_2 was proposed.

2. The first member of the completely methylated β-diacetylene hydrocarbons, with three quaternary carbon atoms, 2,2,5,5,8,8-hexamethylnonadiyne-3,6 (III), was obtained by the reaction of tert.-butylacetylenemagnesium bromide with 2,2,5-trimethyl-5-chlorohexyne-3 (II). The structure of the hydrocarbon was demonstrated by the production of trimethylacetic and dimethylmalonic acids during ozonization.

3. It was found that the propargylation reaction is accompanied by partial cleavage of HCl from the chloride (II), with the formation of the enynic hydrocarbon, 2,5,5-trimethylhexen-1-yne-3 (IV).

4. 2,2,5-Trimethylhexyn-3-ol-5 (I) was obtained from acetone and tert.-butylacetylene by A. E. Favorsky's method, and 2,2,5-trimethyl-5-chlorohexyne-3 (II) was obtained from it by the action of gaseous hydrogen chloride.

* The exposure was 8 hours. The intensity of the lines was evaluated visually on a 5-mark scale.

** The literature values for the dimethylmalonic acid were: m. p. 186° [33], 192-193° [34], 191° [35].

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REACTION OF PHENYLACETYLENE WITH LOWER SATURATED MONOBASIC ACIDS

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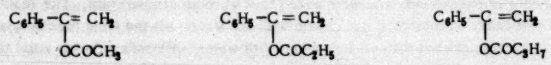
As is known [3] the process of the reaction of acids with acetylene [1] and substituted acetylene hydrocarbons [2] leads to the formation of unsubstituted and substituted vinyl esters, which can polymerize in the presence of catalysts and, consequently, can therefore serve as raw material in the production of synthetic resins.

Esters synthesized from the available initial products have found use in industry. Vinyl acetate, for example, belongs here [4]. The vinyl esters are also obtained by other methods: by the reaction of ketenes with ketones and aldehydes [5], of anhydrides and acid chlorides with ketones and aldehydes [6], of low-molecular vinyl esters with ketones [7], either with other acids or with their anhydrides [8], by pyrolysis of diacetates of α-glycols [9], by treatment of the dibromohydrin of α-glycol, dissolved in glacial acetic acid, with sodium acetate [10].

Because of the practical importance of the vinyl esters to the problems, adequate attention relating to them has been given in the literature; however, the reaction of the saturated monobasic acids and substituted acetylenes has been little investigated. The reason for this is the small availability of the initial hydrocarbons and, obviously, the properties of the esters themselves.

Wishing to fill to some extent the existing gap, we decided to add acetic, propionic and butyric acids to mono-substituted acetylene hydrocarbons, having 8 carbon atoms in the molecule, 6 of which by different methods were combined into one radical. Of the hydrocarbons we chose phenylacetylene as the first object. In the presence of mercuric salts of the acids listed and of a catalyst of boron fluoride, the acids added to it, and the following esters of mono-substituted vinyl esters were isolated:

1-Phenyl-1-acetoxyethene (I), 1-phenyl-1-propionyloxyethene (II) and 1-phenyl-1-butyroxyethene (III):



(I) (II) (III)

All of the esters isolated were colorless, transparent, mobile liquids, possessing a pleasant odor. The first of them (I) proved to be identical to the products synthesized either from acetophenone and the simplest ketene [5] or from acetophenone and 2-acetoxypropene [7], which are described in the literature. In the first fractions of the reaction products we found small quantities of unreacted phenylacetylene in all instances, and in all the fractions, besides the esters, we found acetophenone. Its quantity fluctuated between 10 and 18 g per 0.5 mole of the phenylacetylene. From 16 to 30% of the initial hydrocarbon was converted to ketone. The formation of uninvestigated high-molecular products should be considered as the chief direction of the reaction of phenylacetylene with the acids, in the absence of inert solvents.

The esters which we synthesized readily hydrolyzed in water-alcohol solutions of semicarbazide acetate, whereby their ease of hydrolysis at room temperature diminished from the acetate to the butyrate. We utilized this condition for detecting the position of the acyloxy groups in their molecules. In all three instances, the formation of high yields of only acetophenone semicarbazone, both in the cold and on heating, confirmed the correctness of Formulas (I), (II) and (III) which were attributed to the esters.

EXPERIMENTAL

We synthesized the initial phenylacetylene from ω-bromostyrene [11].

B. p. 28.5-29.5°(5-4 mm), d_0^0 0.9464, d_{20}^{20} 0.9295, d_4^{20} 0.9281, n_D^{20} 1.5478.

1-Phenyl-1-Acetoxyethene [5, 7]

2 g of mercuric oxide, 35 g of glacial acetic acid and 3.5 g of acetic anhydride were heated until the mercuric oxide was dissolved. 1.3 ml of catalyst $BF_3 \cdot O(C_2H_5)_2$ [1] (b. p. 124-126.5°) was added to the cooled solution, and with continuous stirring and cooling, 51 g of phenylacetylene (b. p. 28.5-29.5° at 4 mm) was added. The reaction was completed after 1.3 hours, but the stirring was continued at room temperature for 1.5 hours more, after which the reaction mixture was diluted with ether, washed with water, and with soda solution, and was dried with calcium chloride. On removal of the solvent 70.3 g of reaction products was collected. As a result of 3 vacuum distillations 28.9 g (35.7%) of 1-phenyl-1-acetoxyethene (I) was isolated.

B. p. 89.5-90° (3 mm), d_0^0 1.0894, d_{20}^{20} 1.0724, d_4^{20} 1.0706, n_D^{20} 1.5329.

Found %: C 73.98, 73.70; H 6.15, 6.33. M 156, 158. $C_{10}H_{10}O_2$. Calculated %: C 74.05; H 6.21. M 162.

The high-molecular fraction was largest, and was not subjected to investigation. A small quantity of unreacted phenylacetylene was found in the initial fraction. 10-11 g of acetophenone was detected in the initial and intermediate fractions; its quantity was determined by the formation of the semicarbazone with a m. p. of 201-202° (from alcohol), which gave no melting point lowering in a mixture with an equal quantity of known acetophenone semicarbazone.

Hydrolysis of 1-phenyl-1-acetoxyethene in the presence of semicarbazide acetate. 3.2 g of semicarbazide hydrochloride, and 32 g of potassium acetate, and 7-8 ml of water were heated until the salts were completely dissolved. After addition of 15-17 ml of alcohol and cooling, the solution was separated from the potassium chloride precipitate and was added to 1.00-1.05 g of 1-phenyl-1-acetoxyethene (b. p. 89.5-90° at 3 mm) in a small bottle with a ground-glass stopper. After careful stirring the reaction substance was left either at room temperature for a week or was kept in a thermostat for 2-3 hours at not above 50-90°.

The semicarbazone crystals in this and the following instances had the shape of long needles, but after recrystallization from alcohol they were isolated as lustrous plates with a m. p. of 201-202°. They gave no melting point depression in a mixture with an equal quantity of known acetophenone semicarbazone. The yield at room temperature was 92%, but on heating it was quantitative.

1-Phenyl-1-Propionyloxyethene

1.7 g of mercuric oxide was dissolved in 37 g of propionic acid (b. p. 138-141°, n_D^{22} 1.3860). 1 ml of catalyst $BF_3 \cdot O(C_2H_5)_2$ and 51 g of phenylacetylene were added to it at room temperature. The reaction proceeded with evolution of heat; the reaction substance was cooled with tap water; all the time mechanical stirring was continued. The reaction products were diluted with ether, washed with water, with soda solution until the reaction of the wash water was alkaline, and dried with calcium chloride. On removal of the solvent and by 4 vacuum distillations, 12 g (13.6%) of 1-phenyl-1-propionyloxyethene was isolated.

B. p. 121-121.5° (8 mm), d_0^0 1.0660, d_{20}^{20} 1.0500, d_4^{20} 1.0482, n_D^{20} 1.5250.

Found %: C 74.89, 74.67; H 6.78, 6.87. M 167, 174. $C_{11}H_{12}O_2$. Calculated %: C 74.97; H 6.87. M 176.

Here, as in the preceding synthesis also, the high-molecular fraction was largest, and it was not subjected to investigation. In the first three fractions with a b. p. of about 60-70° (5 mm) unreacted phenylacetylene was detected by reaction with an ammoniacal solution of silver oxide. In the initial and intermediate fractions 12-13 g of acetophenone was determined by its semicarbazone.

Reaction of 1-phenyl-1-propionyloxyethene with semicarbazide acetate. 1.02 g of the ester (with a b. p. of 121-121.5° at 8 mm) was treated with a water-alcohol solution of semicarbazide acetate at room temperature, with heating, as described in the previous experiment. The yield of acetophenone semicarbazone (m. p. 199-201°) in the cold was 84%, but on heating it was quantitative.

1-Phenyl-1-Butyroxyethene

1 ml of catalyst $BF_3 \cdot O(C_2H_5)_2$ and 51 g of phenylacetylene were added to 1.7 g of mercuric oxide dissolved in 44.0 g of butyric acid (b. p. 161-163°), at room temperature. The reaction proceeded with continous stirring and cooling. The reaction products were diluted with ether, washed with water, and with soda solution, and were dried with calcium chloride. After removal of the solvent and after 3 vacuum distillations, 14.1 g (14.8%) of 1-phenyl-1-butyroxyethene was isolated.

B. p. 131.5-132° (9 mm), d_0^0 1.0434, d_{20}^{20} 1.0275, d_4^{20} 1.0258, n_D^{20} 1.5180.

Found %: C 75.66, 75.50; H 7.52, 7.46. M 189, 186. $C_{12}H_{14}O_2$. Calculated %: C 75.76; H 7.42. M 190.

In the present instance, as in the two preceding, the main fraction was an uninvestigated high-molecular fraction. In the 1st fraction, with a b. p. of about 76.5° (9 mm), unreacted phenylacetylene was detected. Acetophenone was found in the 1st and intermediate fractions by the method described earlier.

Reaction of 1-phenyl-1-butyroxyethene-1 with semicarbazide acetate. Under the conditions described in the two preceding cases, 1.00-1.02 g of the ester (b. p. 131.5-132° at 9 mm) was treated with semicarbazide acetate at room temperature for a week, but for 2-3 hours on heating at about 50-90°. The yield of acetophenone semicarbazone (m. p. 200-201°) at room temperature was 63%, but on heating it was quantitative.

SUMMARY

1. Three mono-substituted vinyl esters were described – 1-phenyl-1-acetoxyethene, 1-phenyl-1-propionyloxyethene and 1-phenyl-1-butyroxyethene, of which the last two were described for the first time.

2. The easy hydrolyzability of the esters in the presence of semicarbazide acetate was used as a method of finding the position of the acyloxy groups in their molecules.

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OXIDATION OF VINYLACETYLENE HYDROCARBONS BY ORGANIC PEROXIDES

IV. OXIDATION OF 4,7-DIPROPYLDECADIEN-3,7-YNE-5 BY ACETYL PEROXIDE

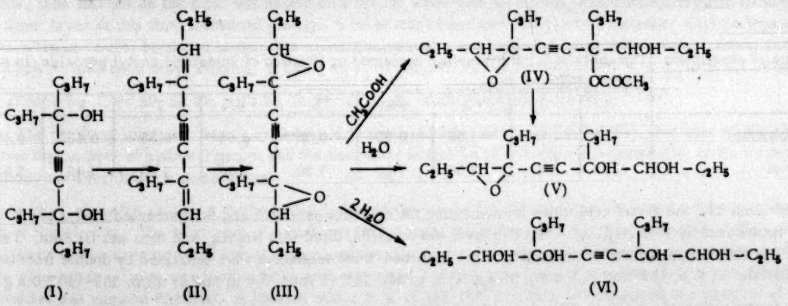
N. M. Malenok and S. D. Kulkina

For the purpose of production of acetylene dioxide and its derivatives, and for the purpose of the study of their properties, we earlier undertook the oxidation of the divinylacetylene hydrocarbon, 3,6-dimethyloctadien-2,6-yne-4, by acetyl peroxide, which gave the vinyl acetylene alcohol-acetate, dioxide and monoxide-alcohol-acetate [1].

In the present work, we oxidized one of the divinylacetylene hydrocarbon homologs by acetyl peroxide.

For its production, the glycol, 4,7-dipropyldecyne-5-diol-4,7 (I), first synthesized from dipropyl ketone and acetylenedimagnesium dibromide, was dehydrated by potassium bisulfate to the divinylacetylene hydrocarbon, 4,7-dipropyldecadien-3,7-yne-5 (II).

Three substances were obtained by oxidation of the hydrocarbon by acetyl peroxide: the acetylene dioxide – 4,7-dipropyl-3,7-dihydroxydecyne-5 (III), the monoxide-alcohol-acetate – 4,7-dipropyl-7-acetoxy-3-hydroxydodecyn-5-ol-8 (IV), and the monoxide-glycol – 4,7-dipropyl-3-hydroxydodecyne-5-diol-7,8 (V).



(I) (II) (III) (IV) (V) (VI)

The monoxide-alcohol-acetate (IV) and the monoxide-glycol (V) were secondary products, which formed on reaction of the dioxide with acetic acid and the dioxide with water. The monoxide-alcohol-acetate (IV) also formed by the action of glacial acetic acid on the dioxide. The monoxide-glycol (V) was obtained on hydrolysis by a saturated solution of sodium carbonate. The acetylene dioxide (III) was hydrolyzed by water to the erythritol, 4,7-dipropyldecyne-5-tetraol-3,4,7,8 (VI). The presence of a triple bond in compounds (III, IV, V) was demonstrated by quantitative bromination.

Thus, for the given compounds we confirmed the fact which we established earlier [1] that the process of oxidation of divinylacetylene hydrocarbons by acetyl peroxide proceeded at the site of the double bonds, but the triple bond remained intact.

EXPERIMENTAL

Synthesis of 4,7-dipropyldecyne-5-diol-4,7 (I). The acetylene glycol was obtained from dipropyl ketone (b. p. 142-144°, 758 mm) and diacetylenemagnesium dibromide. By fractional crystallization of the glycol from ethyl ether its two stereoisomeric forms were isolated, and were recrystallized from methyl alcohol.

One glycol stereoisomer was difficultly soluble in ethyl ether, and had a m. p. of 118-119°.

Found %: C 75.23; H 12.00. $C_{16}H_{30}O_2$. Calculated %: C 75.52; H 11.89.

The second glycol stereoisomer was readily soluble in ethyl ether, and had a m. p. of 124-126°.

Found %: C 75.55, 75.34; H 12.08, 12.14. $C_{16}H_{30}O_2$. Calculated %: C 75.52; H 11.89.

According to the literature [2], the 4,7-dipropyldecyne-5-diol-4,7 with a m. p. of 120° was known.

Dehydration of 4,7-dipropyldecyne-5-diol-4,7 by potassium bisulfate. 29 g of molten potassium bisulfate was added to 81 g of the glycol. Dehydration of the glycol began at once on heating. The water which was split off during 15 minutes was removed in vacuo at 32° (40 mm). 52 g (75%) of the 4,7-dipropyldecadien-3,7-yne-5 (II) was obtained:

B. p. 98-99° (0.5 mm), n_D^{20} 1.4890.

According to the literature [3] the hydrocarbon had a b. p. of 125-127° (18 mm), n_D 1.4890.

Oxidation of 4,7-dipropyldecadien-3,7-yne by acetyl peroxide. 51.8 g of the divinylacetylene hydrocarbon (98-99°, 0.5 mm) was oxidized in an anhydrous ethyl ether medium of 48 g of 76.9% acetyl peroxide (2 moles of the peroxide per 1 mole of the hydrocarbon) at a temperature of −12°. After gradual addition of all the acetyl peroxide to the hydrocarbon, the temperature rose to −9°. The reaction substance was left at room temperature.

We set up a parallel experiment under identical conditions as a control, and the course of the oxidation was checked every day by titration with a 0.1 N solution of $Na_2S_2O_3$. For this, 20 ml of the experimental and control solutions, first diluted by 100 times with water, were taken and the quantity of unreacted acetyl peroxide was determined iodometrically.

The results are cited in the Table, from which it is evident that the oxidation of 4,7-dipropyldecadien-3,7-yne-5 by acetyl peroxide proceeded for 8 days. After this time, a check showed a very negligible change of the acetyl peroxide concentration.

Nature of experiment	Quantity of 0.1 N hyposulfite consumed by titration of unreacted acetyl peroxide (in ml) after number of days:								
	1	2	3	4	5	6	7	8	9
Fundamental	7.50	1.70	1.05	0.85	0.75	0.65	0.55	0.45	0.45
Control	7.50	7.50	7.50	7.50	7.50	7.50	7.45	7.40	7.40

On the ninth day, the acetic acid which formed during the oxidation reaction and the unreacted acetyl peroxide were neutralized by 10% Na_2CO_3. The ether layer was removed, dried with Na_2SO_4, and then was filtered. The ether was removed, and from the substances which remained, three substances were separated by double fractional distillation: 1) b. p. 109-110° (0.5 mm); 35.5 g; 2) b. p. 156-157° (1 mm), 3.0 g; and 3) m. p. 109-110°, 0.8 g.

Investigation of substance with a b. p. of 109-110° (0.5 mm). The liquid was a greenish-yellow color. It dissolved well in ethyl ether, ethyl alcohol, chloroform, benzene, and did not dissolve in water. The substance rapidly liberated iodine from a potassium iodide solution, did not react with methylmagnesium iodide, slowly decolorized a chloroform solution of bromine, and gave positive reactions for the carbonyl group with semicarbazide and with 2,4-dinitrophenylhydrazine.

n_D^{20} 1.4573, d_{20}^{20} 0.9103, MR_D 74.84; calc. 74.37.

Found %: C 76.52, 76.71; H 10.61, 10.52. M 240.9. $C_{16}H_{26}O_2$. Calculated %: C 76.80; H 10.40. M 250.

The substance analyzed was the dioxide, 4,7-dipropyl-3,7-dioxydecyne-5 (III).

The presence of a triple bond in the dioxide was demonstrated by a quantitative bromination.

0.2917 g of the dioxide, dissolved in chloroform, added 0.3513 g of bromine, which also corresponded to the theoretical calculation of the addition of 4 atoms of bromine, or 0.3734 g per triple bond.

Investigation of the substance with a b. p. of 156-157° (1 mm). The viscous liquid dissolved in the same solvents as the dioxide.

n_D^{20} 1.4675, d_{20}^{20} 0.9824, MR_D 87.56; calc. 86.64.

Found %: C 69.53, 69.72; H 9.95, 9.89; OH 6.39. M 305.7. $C_{18}H_{30}O_4$. Calculated %: C 69.68; H 9.68; OH 5.48. M 310.

According to the analytical data, the substance was the monoxide, 4,7-dipropyl-7-acetoxy-3-oxydecyn-5-ol-8 (IV).

The presence of a triple bond in the substance was demonstrated by a quantitative bromination.

0.2078 g of the substance, dissolved in chloroform, added 0.2006 g of bromine. Theoretically, for a triple bond 0.2145 g of bromine should add.

Investigation of the substance with a m. p. of 109-110°. A crystalline substance was isolated from the intermediate 110-135° (0.5 mm) fraction, obtained by distillation of the divinylacetylene hydrocarbon which was oxidized by acetyl peroxide. It was separated from the liquid, and then was washed 3 times with ethyl ether. 0.8 g of the substance with a m. p. of 109-110° was obtained.

Found %: C 71.36, 71.29; H 10.57, 10.53; OH 11.04. M 281. $C_{16}H_{28}O_3$. Calculated %: C 71.64; H 10.45; OH 12.69. M 268.

The resulting 4,7-dipropyl-3-oxydecyne-5-diol-7,8 (V) slowly liberated iodine in an acid medium of potassium iodide. It dissolved poorly in ethyl ether, benzene and in water.

The presence of a triple bond in the oxy-glycol was demonstrated by a quantitative bromination.

0.1040 g of the substance, dissolved in chloroform, added 0.1085 g of bromine. Theoretically, for a triple bond 0.1242 g of bromine must be added.

Hydrolysis of the dioxy-4,7-dipropyl-3,7-dioxydodecyne-5 (III). 21 ml of 1% H_2SO_4 was added to 3.2 g of the dioxide. The mixture in the flask was heated on a boiling water bath for 2 hours, with frequent vigorous shaking. The upper layer at this time thickened greatly. 5 ml of ethyl ether was added to the substance. Crystals separated at the ether and water boundary layer. The crystalline substance was separated, washed 3 times with ether, and then was recrystallized from ethyl alcohol. It had a m. p. of 204-206° in a sealed capillary. 0.93 g (29%) was obtained.

Found %: C 66.93, 66.91; H 10.70, 10.77. $C_{16}H_{30}O_4$. Calculated %: C 67.13; H 10.48.

The resulting substance was an erythritol, 4,7-dipropyldecyne-5-tetraol-3,4,7,8 (VI). We were unable to determine the number of hydroxyl groups and the molecular weight for it, because of its insolubility in the solvents ordinarily used for these determinations.

Action of acetic acid on 4,7-dipropyl-3,7-dioxydodecyne-5 (III). 15 ml of glacial acetic acid was added to 3.5 g of the dioxide. The mixture in the flask was boiled under reflux for 2.5 hours. The unreacted acetic acid was neutralized with a saturated solution of soda; moreover, a viscous, oily layer separated, which was extracted with ether The ether solution was washed twice with water,and dried with sodium sulfate. The ether was removed, and the residue was vacuum distilled. A fraction with a b. p of 153-154° (0.5 mm) was separated in a quantity of 1.8 g (51.4%).

Found %: C 69.74; H 9.97. $C_{18}H_{30}O_4$. Calculated %: C 69.68; H 9.68.

4,7-Dipropyl-7-acetoxy-3-oxydodecyn-5-ol-8 (IV) was obtained, which was also formed by the oxidation of 4,7-dipropyldecadien-3,7-yne-5 (II) by acetyl peroxide.

Saponification of 4,7-dipropyl-7-acetoxy-3-oxydodecyn-5-ol-8 (IV). 0.8 g of the substance (IV) was shaken with a saturated solution of sodium carbonate for 5 hours at 50-60°. The oily layer was extracted with ether and dried with sodium sulfate. After removal of the ether, the residue partially crystallized on the third day. The crystalline substance was separated, washed with ether and recrystallized from methyl alcohol. It had a m. p of 110° and showed no depression on mixture with crystals of the monoxide-glycol (V), obtained by the oxidation of the divinylacetylene hydrocarbon (II) by acetyl peroxide.

SUMMARY

1. On oxidation of 4,7-dipropyldecadien-3,7-yne-5 (II) by acetyl peroxide, we obtained: 4,7-dipropyl-3,7-dioxydodecyne-5 (III); 4,7-dipropyl-7-acetoxy-3-oxydodecyn-5-ol-8 (IV) and 4,7-dipropyl-3-oxydodecyne-5-diol-7,8 (V).

2. The monoxide-alcohol-acetate (IV) was also obtained by the action of acetic acid on the dioxide. The monoxide-glycol (V) was formed by its saponification.

3. On hydrolysis the dioxide (III) gave the acetylenic erythritol, 4,7-dipropyldecyne-5-tetraol-3,4,7,8 (VI).

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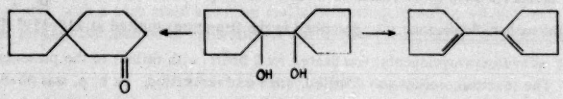
SYNTHESIS OF HYDROCARBONS

L. SYNTHESIS OF 1,1'-DICYCLOPENTENYL

R. Ya. Levina, V. R. Skvarchenko and O. Yu. Okhlobystin

The production of 1,1'-dicyclopentenyl (II) from 1,1'-dihydroxycyclopentyl (I) was complicated by the fact that, on dehydration the latter underwent the pinacoline rearrangement to a considerable degree [1], and two closely-boiling and difficultly-separable reaction products were formed; a hydrocarbon and the corresponding pinacoline, spiro-(4,5)-decanone-6 (III).

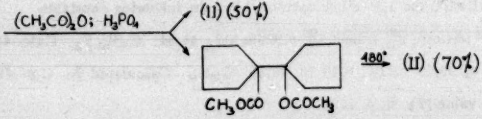


(III) (I) (II)

Thus, in the dehydration of 1,1'-dihydroxydicyclopentyl by anhydrous alum by Barnett and Lawrence [2], they were unable to separate pure 1,1'-dicyclopentenyl and to obtain a satisfactory analysis for it. Zelinsky and Elagina [1] obtained a 78% yield of spiro-(4,5)-decanone-6 by heating 1,1'-dihydroxydicyclopentyl with 50% sulfuric acid.

Our experiments showed that on dehydration of this bicyclic pinacol with 10% sulfuric acid, a mixture of the diene and pinacoline formed which, on the average, contained only about 25% of 1,1'-dicyclopentenyl, but dehydration in the presence of aluminosilicate screenings led to the formation of a mixture, 85% of which consisted of the spirodecanone.

One of the methods of conversion of pinacols to hydrocarbons free of admixtures of the corresponding pinacolines, was a method of pyrolysis of the diacetates of pinacols [3]. This method was used in the present work for the production of 1,1'-dicyclopentenyl. By the pyrolysis of the diacetate of 1,1'-dihydroxydicyclopentyl (IV) at 480°, a 70% yield of 1,1'-dicyclopentenyl was obtained, which contained no pinacoline impurity. However, the yield of the initial diacetate on its production from the dihydroxydicyclopentyl by the action of acetic anhydride in the presence of phosphoric acid did not exceed 25%, since together with the dihydroxydicyclopentyl from acylation, its dehydration proceeded chiefly to the dicyclopentenyl (50% yield).



Thus, from dihydroxydicyclopentyl, 1,1'-dicyclopentenyl free of spirodecanone can be obtained directly by the action of acetic anhydride in the presence of phosphoric acid, and simultaneously by pyrolysis of the diacetate which is formed, the total yield of the dicyclopentenyl can be increased to 66%, on the basis of the initial dihydroxydicyclopentyl. Further, it was found that the dihydroxydicyclopentyl was not acylated by boiling with acetic anhydride without phosphoric acid, but was only dehydrated, and the yield of dicyclopentenyl reached 72% of the theoretical.

Thus, we were able to develop a convenient method of production of 1,1'-dicyclopentenyl, the hydrocarbon which, unlike its six-membered analog, 1,1'-dicyclohexenyl, had been until recently difficultly available and little studied.

A quantitative yield of dicyclopentyl was obtained by the hydrogenation of 1,1'-dicyclopentenyl over platinum

black at room temperature. Earlier [4] one of us carried out the synthesis of this hydrocarbon with the use of cyclopentadiene as the starting material.

The method proposed in the present work (cyclopentanone ⟶ dihydroxydicyclopentyl ⟶ 1,1'-dicyclopentenyl ⟶ dicyclopentyl), enabled us to synthesize dicyclopentyl with a high yield from another available starting material, cyclopentanone.

EXPERIMENTAL

Dehydration of 1,1'-dihydroxydicyclopentyl with 10% sulfuric acid and aluminosilicate screenings. 25 g of 1,1'-dihydroxydicyclopentyl (m. p. 108-109°; obtained by N. D. Zelinsky and N. V. Elagina's method [1]) and 125 ml of 10% sulfuric acid were refluxed for 4 hours; the reaction product was steam-distilled, dried with calcium chloride and vacuum distilled. A mixture of 1,1'-dicyclopentenyl and spiro-(4,5)-decanone-6 with a b. p. of 75-90° (8 mm) and n_D^{20} 1.4960 was obtained. An analysis for the carbonyl group content [5] showed that the resulting mixture contained 74.5% of the spiro ketone. In order to remove the 1,1'-dicyclopentenyl the mixture was heated with maleic anhydride and the precipitate was filtered off. Pure spiro-(4,5)-decanone-6 was isolated from the filtrate by vacuum distillation.

B. p. 86-87° (10 mm), n_D^{20} 1.4849, d_4^{20} 0.9889.

Literature values for spiro-(4,5)-decanone-6 [1] were: b. p. 99-100° (13 mm), n_D^{20} 1.4849, d_4^{20} 0.9890.

The 2,4-dinitrophenylhydrazone (not described in the literature) melted at 118-119° (from alcohol).

25 g of 1,1'-dihydroxydicyclopentyl was heated for 2 hours (with reflux) in the presence of aluminosilicate screenings (3 g). The reaction product was distilled, dried and redistilled: its b. p. was 80-88° (10 mm), n_D^{20} 1.4880; judging by an analysis for the carbonyl group content, 85% of it consisted of the spirodecanone.

Acetylation and dehydration of 1,1'-dihydroxydicyclopentyl by the action of acetic anhydride in the presence of phosphoric acid. A mixture of 3 g of concentrated phosphoric acid and 30 g of acetic anhydride prepared a day before the beginning of the reaction was added, with constant stirring, to 100 g of 1,1'-dihydroxydicyclopentyl and 300 g of freshly-distilled acetic anhydride, placed in a three-necked flask, equipped with a reflux condenser, stirrer and thermometer. The reaction substance was stirred for 5 hours at 42-45° and then was poured into water. The solution was saturated with soda until the reaction was alkaline; the upper layer (1,1'-dicyclopentenyl with suspended diacetate crystals) was separated, and the diacetate crystals were filtered off. The aqueous layer was extracted three times with ether, and the dicyclopentenyl which formed was added to the ether extract; the ether solution was washed with water until neutral, and was dried with sodium sulfate. After removal of the ether and vacuum distillation of the residue, 39.5 (50%) of 1,1'-dicyclopentenyl with a b. p. of 77.5-79° (9 mm), and the diacetate of 1,1'-dihydroxydicyclopentyl (the 120-128° fraction at 9 mm) were obtained. The latter crystallized immediately in the vessel. A total of 35.6 g (23.8%) of the diacetate with a m. p. of 118-118.5° was obtained (from petroleum ether).

Found %: C 66.0, 66.08; H 25.18, 25.20. $C_{14}H_{22}O_4$. Calculated %: C 66.12; H 25.16.

The diacetate of 1,1'-dihydroxydicyclopentyl was not described in the literature.

After distillation the 1,1'-dicyclopentenyl had the following constants:

B. p. 78.5° (8 mm), n_D^{20} 1.5268, d_4^{20} 0.9259; MR_D 44.54. $C_{10}H_{14}F_2$. Calc. 43.05. EM_D 1.49.

Found %: C 89.60, 89.50; H 10.70, 10.65. $C_{10}H_{14}$. Calculated %: C 89.49; H 10.51.

Literature value [2]: b. p. 208°.

The pyrolysis of the diacetate of 1,1'-dihydroxydicyclopentyl was carried out in a tube (diameter 20 mm and length 70 cm), filled with glass wool, at 480°, in a weak current of nitrogen; the diacetate was introduced at the rate of 30 g per hour (the vessel was cooled with solid carbon dioxide). The resulting hydrocarbon was washed with water, soda, and again with water until the reaction was neutral, dried with calcium chloride and vacuum distilled. Its b. p. was 78-79° (9 mm), n_D^{20} 1.5248.

The yield of the dicyclopentenyl amounted to 70%.

Dehydration of 1,1'-dihydroxydicyclopentyl by acetic anhydride. 80 g of the dihydroxydicyclopentyl and 100 g of acetic anhydride were boiled under reflux for 5 hours, after which the reaction substance was poured into water. The solution was saturated with soda and extracted with ether; the ether extract was washed with water until it was neutral, dried with calcined potash and the ether was removed. 42 g (72%) of 1,1'-dicyclopentenyl was obtained by

vacuum distillation of the residue. Its b. p. was 77° (8 mm), n_D^{20} 1.5240.

Hydrogenation of 1,1'-dicyclopentenyl. 1,1'-Dicyclopentenyl (10 g of the hydrocarbon in 50 ml of alcohol) was hydrogenated over platinum black at room temperature. The alcohol was washed out with water, and the hydrocarbon was dried with calcium chloride and vacuum distilled. The resulting dicyclopentyl (10 g; its yield was quantitative) had the following constants:

B. p. 66.5° (12 mm), n_D^{20} 1.4655, d_4^{20} 0.8668; MR_D 43.96. $C_{10}H_{18}$. Calc. 43.98.

Literature values: b. p. 188-190°, n_D^{20} 1.4654, d_4^{20} 0.8665 [6], b. p. 188° (765 mm), 57° (8 mm), n_D^{20} 1.4648, d_4^{20} 0.8669 [4].

SUMMARY

1. The following methods of production of 1,1'-dicyclopentenyl, which contained no admixtures of the pinacoline, spiro-(4,5)-decanone-6, were developed: dehydration of 1,1'-dihydroxydicyclopentyl by acetic anhydride in the presence of phosphoric acid at 45° (50% yield); dehydration of 1,1'-dihydroxydicyclopentyl by acetic anhydride at 140° (72% yield); pyrolysis of the diacetate of 1,1'-dihydroxydicyclopentyl at 480° (70% yield).

2. Dicyclopentyl was obtained by the hydrogenation of 1,1'-dicyclopentenyl. The method developed enabled us to synthesize dicyclopentyl, with a high yield and from available starting material, which is also why it could be proposed as a convenient preparative method of production of this hydrocarbon.

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SYNTHESIS AND POLYMERIZATION OF NITROGEN-CONTAINING SUBSTITUTED STYRENES

M. M. Koton, Yu. V. Mitin and F. S. Florinsky

It is known that the capacity toward polymerization of the substituted styrenes changes [1], depending on the nature of the substituent and its position in the benzene ring of styrene. Nitrogen-containing styrene derivatives are of special interest in this respect. Thus, for the nitrostyrenes it was shown that p-nitrostyrene polymerizes readily, but o-nitrostyrene does not polymerize at all [2]; a readily polymerizing compound is obtained by the introduction of the cyano-group into styrene [3]. Because of the fact that systematic investigations of the polymerizability of nitrogen-containing styrene derivatives are lacking in the literature, we synthesized p-cyanostyrene, p-nitrostyrene, p-aminostyrene and p-dimethylaminostyrene, and studied the process of their thermal polymerization in bulk. p-Nitrostyrene and p-cyanostyrene polymerized very readily, which enabled us to study their polymerization kinetics at 50-100°. Thus, for example, after 3 hours at 98°, p-nitrostyrene formed 46% of polymer (Fig. 1) and p-cyanostyrene after 4 hours at 100° formed 34% (Fig. 2). The p-nitrostyrene polymer was a clear yellow color, and the p-cyanostyrene polymer was transparent; colorless; neither dissolved in the usual organic solvents.

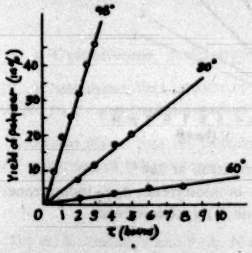

Fig. 1. Polymerization of p-nitrostyrene

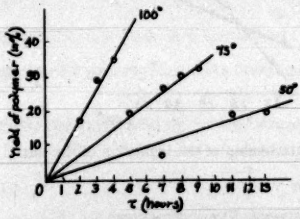

Fig. 2. Polymerization of p-cyanostyrene.

Polymerization at 100°

Name of monomer	Yield of polymer (in %) with duration of polymerization		
	3 hours	5 hours	7 hours
Styrene	7.1	11.5	15.5
p-Aminostyrene	3.0	6.0	8.2
p-Dimethylamino-styrene	–	9.0	17.6

Unlike p-nitrostyrene, p-aminostyrene polymerized with great difficulty; only at 150° was an appreciable formation of the polymer observed. The p-aminostyrene polymer was a clear, brown color and was very brittle. The polymerization of p-dimethylaminostyrene proceeded unusually: at 120-130° it polymerized more readily than did p-aminostyrene, but with an increase of the temperature to 150°, decomposition of the substance with evolution of volatile lower aliphatic amines was observed (see Table).

The processes of polymerization of p-nitrostyrene and p-cyanostyrene were reactions of the 1st order, and the energy of activation of the polymerization process for the former was equal to 21,000 ± 1,000 and for the latter was 8,200 ± 200 kcal/mole (Fig. 3).

Comparing the polymerization rate (at 100°) of p-cyanostyrene with that of the halostyrenes and of p-nitrostyrene (Figs. 1, 2, 4) we obtained the following relationship:

$$p\text{-CN} > p\text{-I} > p\text{-Br};\quad p\text{-NO}_2 > p\text{-CN}.$$

Consequently, p-cyanostyrene has the highest polymerization rate (and the lowest activation energy value), compared with the halostyrene homologous series. Comparing the polymerization rate of p-cyanostyrene with the polymerization rate of p-nitrostyrene, it is necessary to note the significant effect of the temperature factor. p-Cyanostyrene polymerized more rapidly at 50-60° than did p-nitrostyrene; at 75-80°, the rates were equal, and at 98-100°, the p-nitrostyrene polymerized 1.5 times more rapidly than did the p-cyanostyrene.

EXPERIMENTAL

The synthesis of p-nitrostyrene was carried out according to the scheme of [4, 5]:

$$C_6H_5Br \xrightarrow[(CH_2)_2O]{Mg} C_6H_5CH_2CH_2OH \xrightarrow{PBr_3} C_6H_5CH_2CH_2Br \xrightarrow{HNO_3} p\text{-}O_2NC_6H_4CH_2CH_2Br \xrightarrow{-HBr}$$
$$\longrightarrow p\text{-}O_2NC_6H_4CH = CH_2.$$

200 g of phosphoric tribromide was added to 238 g of phenyl ethyl alcohol, and allowed to stand overnight, and decomposed with water; the organic layer was separated, washed, dried and vacuum distilled. 281 g (76%) of the phenyl ethyl bromide with a b. p. of 91-93° (11 mm) was obtained, which was nitrated at −5° with a mixture of acetic acid, acetic anhydride and fuming nitric acid. A yellow crystalline precipitate of p-nitrophenyl ethyl bromide with a m. p. of 69° was separated. Its yield was 53%.

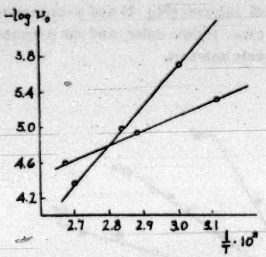

Fig. 3. Relationship of the logarithm of the initial rate (log v_0) to $\frac{1}{T}$.

1) p-Nitrostyrene; 2) p-cyanostyrene.

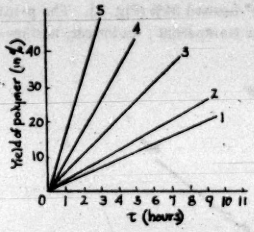

Fig. 4. Polymerization at 100°.

1) Styrene; 2) p-bromostyrene; 3) p-iodostyrene; 4) p-cyanostyrene; 5) p-nitrostyrene.

150 ml of triethanolamine, 80 ml of water and 25 g of p-nitrophenyl ethyl bromide were placed in a round-bottomed flask. The mixture was heated to boiling; moreover, the p-nitrostyrene was steam-distilled as a heavy yellow liquid, which crystallized on standing. After recrystallization from hexane at −30°, its m. p. was 23° (21.4° [6]). Its yield was 10 g (62%).

Found %: N 10.39. $C_8H_7O_2N$. Calculated %: N 10.53.

The synthesis of p-cyanostyrene was carried out according to the scheme of [7]:

$$p\text{-}BrC_6H_4Br \xrightarrow[CH_3CHO]{Mg} p\text{-}BrC_6H_4CH(OH)CH_3 \xrightarrow{CuCN} p\text{-}CNC_6H_4CH(OH)CH_3 \xrightarrow{-H_2O} p\text{-}CNC_6H_4CH = CH_2.$$

p-Bromophenylmethylcarbinol with a b. p. of 144-145° (20 mm) and a yield of 40% was obtained from 14 g of magnesium, 118 g of p-dibromobenzene and 15 g of acetaldehyde in absolute ether. 120 g of p-bromophenylmethylcarbinol, 110 ml of dry pyridine, 60 g of freshly-prepared cuprous cyanide, 2 g of hydroquinone, several crystals of copper sulfate and several drops of p-tolylnitrile (as catalysts of the reaction) were placed in a round-bottomed flask. The mixture was boiled for 15 hours at 200-215° and the hot solution was poured into an aqueous solution of ammonia. We extracted with benzene and ether, washed repeatedly (at the rate of 200 ml) with dilute ammonia, with dilute hydrochloric acid, with water and with a saturated solution of sodium chloride. The liquid was dried, the solvent was removed, and the liquid was vacuum distilled. p-Cyanophenylmethylcarbinol with a b. p. of

135-140° (5 mm), n_D^{20} 1.5480 (1.5477 [7]) was obtained. Its yield was 20.7 g (24%). The resulting carbinol was dehydrated over activated, granulated aluminum oxide at 300-325° (100-110 mm). The vessel was cooled with solid carbon dioxide. The resulting condensate was dissolved in ether, and washed with a 10% solution of sodium hydroxide and with a saturated solution of calcium chloride. The liquid was dried, the ether was removed, and the residue was vacuum distilled. The p-cyanostyrene was a colorless liquid with the odor of styrene, its b. p. was 104° (10 mm), n_D^{20} 1.5782 (1.5781 [7]). Its yield was 46%.

Found %: N 10.22. C_9H_7N. Calculated %: N 10.85.

Synthesis of p-aminostyrene. p-Aminostyrene was synthesized by P. P. Shorygin and N. V. Shorygina's method [8] as pale-yellow crystals with a m. p. of 20-22° (22° [8]). Their yield was 55%).

Synthesis of p-dimethylaminostyrene. p-Dimethylaminostyrene was synthesized by the scheme of [9]:

$$CH_3MgBr + (CH_3)_2NC_6H_4CHO \longrightarrow (CH_3)_2NC_6H_4CH(OH)CH_3 \xrightarrow{-H_2O} (CH_3)_2NC_6H_4CH = CH_2.$$

A Grignard reagent prepared from 12.5 g of magnesium and 40 g of methyl bromide in ether, and a solution of 50 g of dimethylaminobenzaldehyde in a mixture of ether and benzene was added. We stirred the reaction mixture for 1 hour and decomposed it with a saturated solution of ammonium chloride in a 1% solution of hydrochloric acid. The organic layer was separated, washed, dried and distilled. The p-dimethylaminostyrene was a colorless liquid with a b. p. of 89° (2.5 mm), a m. p. of 16°, n_D^{20} 1.6045 (m. p. of 16°, n_D^{24} 1.6032 [9]). Its yield was 14 g (25%).

Polymerization. The polymerization of the monomers synthesized was carried out in sealed glass ampoules in a thermostat with accurate regulation of the temperature (± 0.05°). For the determination of the p-nitrostyrene polymer yield, a method of cold extraction of the monomer with acetone was used. For the determination of the p-cyanostyrene polymer yield, the method of bromination of the unreacted monomer was used.

SUMMARY

1. p-Cyanostyrene, p-nitrostyrene, p-aminostyrene and p-dimethylaminostyrene were synthesized.

2. It was shown that introduction of cyano- and nitro-groups into the para-position of the benzene ring of styrene led to a considerable increase of the polymerization rate.

3. It was shown that the introduction of amino- and dimethylamino-groups into the benzene ring of styrene led to a reduction of the polymerization rate.

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OZONIZATION OF UNSATURATED COMPOUNDS

1. OBTAINING OZONE ABSORPTION CURVES FOR UNSATURATED COMPOUNDS

A. I. Yakubchik, N. G. Kasatkina and T. E. Pavlovskaya

The ozonization and subsequent decomposition of the ozonides of unsaturated compounds leads mostly to the breaking of the carbon chain at the multiple bond, and to the formation of carbonyl- and carboxyl-containing substances [1]. However, in the ozone cleavage products of a series of unsaturated compounds, substances were found which could not be obtained by the usual scheme of ozonolysis [2]. For example, on ozonization of phenyl crotyl ether $CH_3CH=CHCH_2OC_6H_5$, together with acetic acid, formic acid formed; on ozonization of methylvinylcarbinol $CH_3CHOHCH=CH_2$, together with formic acid, acetic acid was also obtained. The anomalous products of the decomposition of the ozonides can lead to erroneous conclusions concerning the position of the multiple bonds in the substance studied. A more reliable idea of the structure of unsaturated compounds could be obtained by the study of ozone absorption curves.

The ozonization curves of some unsaturated compounds were obtained by Brus and Peyresblanques [3]. They found that the rate of addition of ozone to substances with a triple bond was less than that of compounds with a double bond, but was greater than the rate of ozonization of aromatic compounds. Some groups [4], as, for example, the $>C=O$ group in conjugation with a double bond, some phenyl groups, or two chlorine atoms combined with carbon atoms at a double bond, retard the rate of addition of ozone. The rate of ozonization of methylated benzene homologs [5] changes in relation to the number of methyl groups replacing hydrogen in the benzene ring, therefore hexamethylbenzene ozonized more rapidly than did mesitylene, and the latter ozonized more rapidly than did m-xylol.

We developed a simple method of calculation of the quantity of ozone absorbed by unsaturated compounds, and a simple method of obtaining ozone absorption curves. The curves, obtained several times for the same substance, reproduced well. The curves of absorption of ozone by the ethylenes (Fig. 1, Curve 1; Fig. 2, Curve 1), diethylene compounds with isolated double bonds (Fig. 1, Curve 3), and acetylene compounds (Fig. 1, Curve 4) have one section corresponding to the addition of ozone at a constant or slowly diminishing rate.

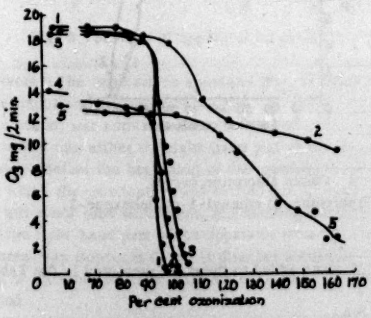

Fig. 1. Ozone absorption curves.
1) Tetramethylethylene; 2) elaidic acid; 3) biallyl; 4) dimethylacetylene; 5) diphenylacetylene.

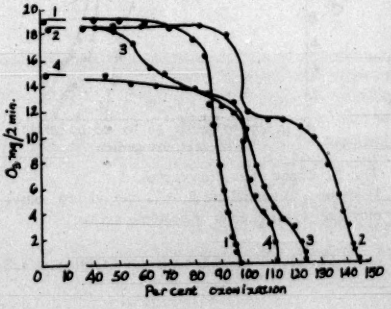

Fig. 2. Ozone absorption curves.
1) Allyl alcohol; 2) 2-methylhepten-2-one-6; 3) 4,6-dimethylmenthadiene-6,8; 4) tert.-butylacetylene.

In a number of instances the quantity of ozone added agreed with the calculated quantity (Fig. 1, Curve 4; Fig. 4, Curve 1, etc.); in other instances more ozone was added than resulted from calculation. An excessive quantity of ozone added, for example, to substances containing the $\rangle C=O$ group (Fig. 3, Curve 4; Fig. 2, Curve 2). An additional quantity of ozone was consumed for the oxidation of the $\rangle C=O$ group [3, 6], therefore the quantity of ozone used for the oxidation of this group was less than the calculated. This is explained by the fact that the $\rangle C=O$ group is oxidized not only by ozone, but also by oxygen under the influence of the catalytic action of ozone [7], therefore oxidation proceeds at a much lower and at a diminishing rate. The carboxyl group of the lower acids [8] reacts with ozone more difficultly than do aldehydic or ketonic groups; however, if the acid has a long carbon chain with an ethylene bond, no reaction of ozone with the carboxyl group occurs (Fig. 1, Curve 2).

A greater quantity of the ozone than the calculated was absorbed in the ozonization of hydrocarbons containing a tert.-butyl radical, for example, methyl-tert.-butylethylene (Fig. 3, Curve 3), tert.-butylacetylene (Fig. 2, Curve 4), and 4,6-dimethylmenthadiene-6,8 (Fig. 2, Curve 3).

We obtained ozone absorption curves which had a discontinuity for a series of unsaturated compounds. The ozone absorption curve of styrene (Fig. 3, Curve 1) had two sections which corresponded to different rates. The section with the greater rate corresponded to the addition of ozone to the ethylene bond, and the section with the lower rate corresponded to the addition of ozone to the benzene ring. A similar curve was obtained for diphenylacetylene (Fig. 1, Curve 5).

The ozone absorption curves of hydrocarbons containing two double bonds, one of which is in the ring, also has a discontinuity (Fig. 4, Curve 2; Fig. 2, Curve 3). The double bonds of such hydrocarbons add ozone at different rates. A decrease of the rate sets in after absorption of 50% of the amount of ozone calculated for addition of two double bonds.

From a consideration of the ozone absorption curves of compounds containing a conjugated system of double bonds, it follows that one molecule of ozone adds at a greater rate, and the second at a lower and diminishing rate (Fig. 3, Curve 2; Fig. 4, Curve 1). Harries [9] observed that compounds containing conjugated double bonds add the first ozone molecule more rapidly than the second. For bivinyl it was shown that, on ozonization of the conjugated system of double bonds, the ozone added in the 1,2-position [10].

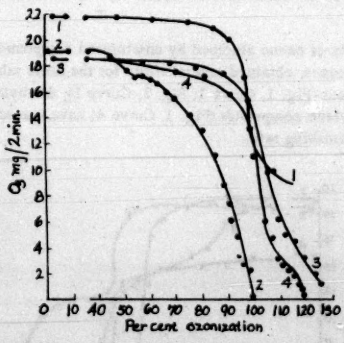

Fig. 3. Ozone absorption curves.
1) Styrene; 2) hexadiene-2,4; 3) methyl-tert.-butyl-ethylene; 4) ethyl ester of crotonic acid.

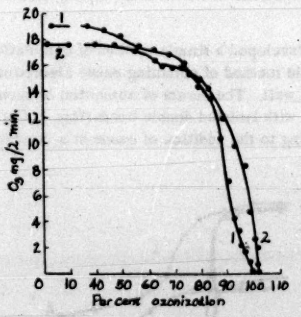

Fig. 4. Ozone absorption curves.
1) Piperylene; 2) ethenyl-1-cyclohexene-3.

The properties of the ozonized substances and the quantity of ozone added to them are presented in the Table.

EXPERIMENTAL

In all the experiments, the ozonization of the unsaturated compounds was carried out under identical conditions. A constant ozone concentration for obtaining the ozonization curves was assured by a constant voltage in the primary winding of the transformer and by a constant rate of passage of the oxygen. In our experiments, the ozone concentration in the ozonized oxygen amounted to 5%. The ozonization was carried out at 0°. Chloroform was used as the

Figure	Curve	Substance	Boiling point	Per cent of ozone added
1	1	Tetramethylethylene	71.5-72°	96.2
1	2	Elaidic acid	50-51 (m. p.)	–
1	3	Biallyl	58-59	104.9
1	4	Dimethylacetylene	27-28	101.5
1	5	Diphenylacetylene	59.5-60 (m. p.)	–
2	1	Allyl alcohol	95-96.5	97.4
2	2	2-Methylhepten-2-one-6	57-57.5 (10 mm)	144.9
2	3	4,6-Dimethylmenthadiene-6,8	88-89 (17 mm)	125.0
2	4	Tert.-butylacetylene	38.5-39	112.1
3	1	Styrene	33-33.5 (10 mm)	–
3	2	Hexadiene-2,4	81.5-82	100.0
3	3	Methyl-tert.-butylethylene	77.5-78	126.1
3	4	Ethyl ester of crotonic acid	137-138	119.3
4	1	Piperylene	41-42	99.2
4	2	Ethenyl-1-cyclohexene-3	65-66 (100 mm)	100.7

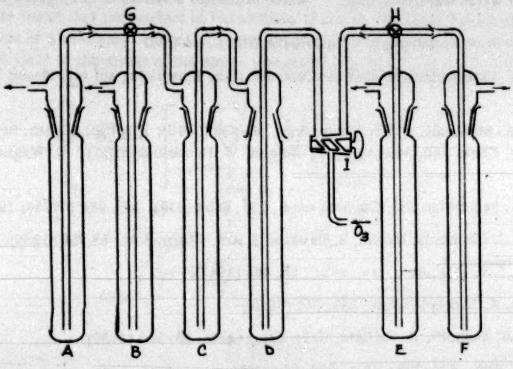

Fig. 5. Scheme of apparatus for obtaining ozone absorption curves.

solvent. The ozonization apparatus (Fig. 5) consisted of test tubes with ground-glass stoppers, equipped with tubes for the imput and discharge of the gas. All connections in the apparatus were made by sections. The oxygen, containing the ozone, was admitted from the ozonizer into the ozonization apparatus. By means of Stopcock I, the gas could be directed into either the right-hand part of the apparatus, in which the ozone content was determined in the ozonized oxygen before the beginning of the experiment, or into the left-hand part of the apparatus, where D was a test tube in which the ozonization was carried out, C was a trap, B was a test tube with a solution of potassium iodide, * and A was a test tube with water, representing the same resistance for the gas current as the potassium iodide solution. In the right-hand part of the apparatus were the test tube E with a potassium iodide solution and test tube F with water. Three-way stopcocks G and H directed a current of gas into either the test tubes with potassium iodide solutions (B and E), or into the test tubes with water (A and F). The gas discharging from the side tubes proceeded into the exhaust hood.

Data for the construction of the ozone absorption curves were obtained as follows: the ozone in the gas entering the vessel in which the ozonization was carried out was determined by titration with thiosulfate of the iodine which formed on passage of the ozone through the potassium iodide solution for 2 minutes. After determination of the

* The potassium iodide solution contained a buffer mixture consisting of mono- and di-substituted sodium phosphates.

initial ozone content in the right-hand part of the apparatus, by turning Stopcock I the gas was directed into the left-hand part of the apparatus, and during the entire ozonization process was passed through the solution of the substance being ozonized. By Stopcock G the gas which was not absorbed by the substance was directed in turn for 2 minutes into test tube A with water. The ozone which added to the substance was calculated from the difference between the ozone content in the gas entering the apparatus (determination in test tube E) and the ozone content in the gas exhausted from the apparatus (determination in test tube B). The end of ozonization came then, when this difference decreased to zero. The total quantity of ozone added could be calculated by adding up the milligrams of ozone absorbed after each 2 minutes for the total process.

SUMMARY

1. A method of obtaining the ozone absorption curves of unsaturated compounds was developed. This method offered the possibility of determining the end of ozonization, of calculating the number of multiple bonds in the ozonized substance from the quantity of ozone added, and of adding any previously calculated quantity of ozone.

2. Ozone absorption curves were obtained for unsaturated compounds containing one or several isolated double bonds, or double bonds occurring in conjugation.

3. Ozone absorption curves of unsaturated compounds containing double bonds and the $>C=O$ group, double bonds and the benzene ring, and triple bonds, were obtained.

4. Ozone absorption curves which had sections corresponding to different rates of absorption of ozone were obtained for unsaturated compounds which contained, together with a double or triple bond, a benzene ring, two double bonds, one of which was in the ring, which contained a system of conjugated double bonds.

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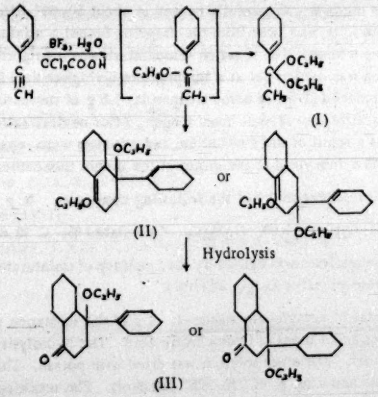
MONOVINYLACETYLENE HOMOLOGS

IV. CYCLIC DIENIC ETHERS

I. A. Favorskaya and I. N. Makarova

The condensation of the dienic ethers of 1-α-methoxyvinylcyclohexane and 1-α-methoxyvinylcyclopentene with p-benzoquinone and p-xyloquinone was studied earlier [1]. In the present work we attempted to synthesize the cyclic dienic ether, 1-α-ethoxyvinylcyclohexene. Furthermore, we proposed to carry out the condensation of this ether with p-xyloquinone, since the reaction product of α-methoxyvinylcyclohexene with p-xyloquinone was a liquid and we did not characterize it in the previous work.

The initial enynic hydrocarbon, 1-acetylenyl-Δ^1-cyclohexene, was obtained from 1-acetylenylcyclohexanol-1 by its reaction with phosphorus oxychloride in pyridine [2]. In a study of the addition reaction of completely anhydrous ethyl alcohol to 1-acetylenyl-Δ^1-cyclohexene in the presence of a catalyst of boron trifluoride, mercuric oxide and trichloroacetic acid, we found that the product of the addition of two molecules of the alcohol to the hydrocarbon triple bond, the diethyl ketal of 1-acetylcyclohexene (I), was obtained in a negligible yield of 6%, but the chief reaction product was a 70% yield of the dimer of the dienic monoether (II).

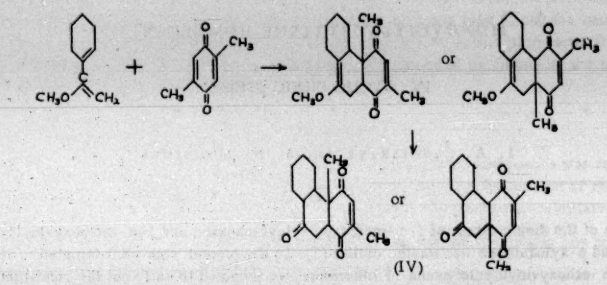


Under the conditions specified, the ethyl alcohol adds less vigorously to the triple bond of the hydrocarbon than does methyl, since in the series of experiments the unreacted enynic hydrocarbon was recovered unaltered, which was not observed in the addition of methyl alcohol under similar conditions. The recovered hydrocarbon was hydrogenated over platinum black, a curve characteristic of the vinylacetylene hydrocarbons being obtained.

The facts presented above confirmed the scheme of addition of alcohols to the enynic hydrocarbons, which one of us, together with Fedorova, proposed [1]. According to this scheme the yield of the dimer in the addition reaction depended on the rates of two competitive reactions, the reaction rate of the dimerization of the initially formed dienic ether and the reaction rate of the addition of the second molecule of alcohol to the dienic ether. Apparently, since the second molecule of ethyl alcohol added rather slowly, the dimer was the main product of the reaction.

As a consequence of the fact that we found that the yield of the diethyl ketal of acetylcyclohexene reached only a few per cent, we were unable to use the unsaturated ketal for the synthesis of 1-α-ethoxyvinylcyclohexene.

For condensation with p-xyloquinone, the α-methoxyvinylcyclohexene synthesized earlier [1] was used. Since the resulting addition product, the assumed methoxy diketone, was a liquid, it was hydrolyzed in an acid medium and was characterized as the tricyclic triketone (IV).



(IV)

For compound (IV) the absorption curve was taken by an SF-11 spectrophotometer (Beckman arrangement) $\lambda_{max.}$ 241 mμ, log ε 4.01 [1, 3-5]. The absence of an absorption maximum in the 290 mμ region, characteristic of the hydroquinones [3, 6], enabled us to ascribe to the compound investigated the structure of the tricyclic triketone, containing the chromophoric group of the α,β-unsaturated diketone.

EXPERIMENTAL

Addition of ethyl alcohol to 1-acetylenylcyclohexene-1. 0.75 ml of a catalyst of boron trifluoride, 2.5 g of red mercuric oxide, 3 ml of completely anhydrous ethyl alcohol [7] and 2 crystals of trichloroacetic acid were placed in a three-necked flask equipped with a mechanical stirrer, thermometer, dropping funnel, reflux condenser, and a closed tube with anhydrone. The mixture was carefully heated at about 50-60°, after which 50 ml of completely anhydrous ethyl alcohol was added to it, and later from the dropping funnel a mixture of 35 g of the hydrocarbon and 50 ml of alcohol was added during 3 hours. The reaction temperature was regulated by cooling the flask in a bath with water. The addition reaction was carried out at a temperature no higher than 20-25°. After 3 hours, an additional portion of the catalyst was introduced (1 ml of boron trifluoride, 1.5 g of mercuric oxide) into the reaction mixture, after which the mixture was stirred for several hours longer. After neutralization by sodium ethylate, the ethyl alcohol was vacuum distilled. As a result of the distillation, two products were separated, a 6% yield of the diethyl ketal of acetylcyclohexene (I) and a 70% yield of the dimer of the dienic monoether (II).

The diethyl ketal of acetylcyclohexene-1 had the following constants: b. p. 73° at 3 mm, n_D^{20} 1.4553.

Found %: C 73.18; H 11.11; C_2H_5O 44.90. $C_{12}H_{22}O_2$. Calculated %: C 72.68; H 11.13; C_2H_5O 45.38.

A certain discrepancy of the analyses was caused by the impurity of unsaturated ketone, the presence of which in the ketal was confirmed spectroscopically ($\lambda_{max.}$ 233 mμ).

Hydrolysis of the diethyl ketal of acetylcyclohexene-1. 2 g of the substance was shaken in a test tube for several minutes with 6 ml of water and 4 drops of hydrochloric acid. The hydrolysis products were salted out with potash and were extracted with ether. The ether solution was dried with potash. The b. p. was 89° at 18 mm, n_D^{20} 1.4907 [8]. The semicarbazone had a m. p. of 218-220° (alcohol). The resulting data agreed with the literature values for acetylcyclohexene. A test of a mixture of the resulting semicarbazone with the known preparation gave no depression.

The dimer (II) was a very viscous, yellowish liquid. Its b. p. was 136-138° (0.02 mm). Because of the difficulty of purification of such a viscous liquid the dimer (II) was converted to the corresponding ketone (III), which was identified as the semicarbazone.

Hydrolysis of the dimer (II). 20 g of the dimer was shaken for 2 hours in a hydrogenation duck with 25 ml of a 5% hydrochloric acid. The ketone was distilled under high vacuum.

B. p. 112-117° at 0.02 mm; n_D^{20} 1.5239.

Found %: C 77.56; H 10.57; C_2H_5O 13.9. M 263.98. $C_{18}H_{28}O_2$. Calculated %: C 78.21; H 10.21; C_2H_5O 16.28. M 276.4.

The semicarbazone of the ketone (III). Its m. p. was 232° (alcohol).

Found %: N 12.55; C_2H_5O 13.69. $C_{19}H_{31}O_2N_3$. Calculated %: N 12.60; C_2H_5O 13.49.

Addition of α-methoxyvinylcyclohexene to p-xyloquinone. 2 g of the dienic ether and 0.7 g of xyloquinone in 20 ml of anhydrous benzene were heated at 100° for 24 hours in a sealed tube. The color of the solution in the tube at the end of the heating had changed from dark-brown to pale-yellow. The contents of the tube were poured into the hydrogenation duck and 20 ml of 10% hydrochloric acid was added, then the duck was shaken for 3 hours. The hydrolysis product, the triketone (IV), consisted of crystals of a pale-lemon color, and after recrystallization from alcohol, the m. p. was 135°. The yield was 40%.

Found %: C 73.86; H 7.92. M 254.5. $C_{16}H_{20}O_3$. Calculated %: C 73.82; H 7.74. M 260.3.

For the assumed triketone an absorption curve was taken by an SF-11 spectrophotometer (Beckman arrangement); $\lambda_{max.}$ 241 mμ, log ε 4.01 (c 0.000403–0.000102 M.), and the solvent was ethyl alcohol.

SUMMARY

1. It was shown that by the reaction of 1-acetylenylcyclohexene-1 with ethyl alcohol in the presence of $BF_3 \cdot (C_2H_5)_2O$, HgO and CCl_3COOH, the dimer of the dienic monoether of 1-α-ethoxyvinylcyclohexene was obtained as the chief reaction product.

2. The diene condensation reaction of 1-α-methoxyvinylcyclohexene with p-xyloquinone was studied.

3. The spectroscopic investigation data enabled us to attribute to the product of the hydrolysis of the resulting addition product a tricyclic triketone structure (3,12-dimethyl-Δ^2-dodecahydro-1,4,9-triketophenanthrene or 2,11-dimethyl-Δ^2-dodecahydro-1,4,9-triketophenanthrene).

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* T. p. = C. B. Translation pagination.

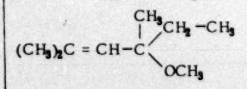
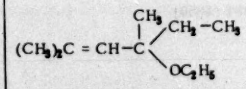
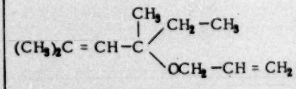
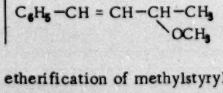
PRODUCTION OF SOME ETHERS WITH AN ALLYL POSITION DOUBLE BOND

V. I. Pansevich-Kolyada, Z. B. Idelchik and L. A. Kureichik

As is known, the action of sulfuric acid on alcohols is the most widely prevalent method of production of ethers. The nature of the alcohols and of the alcoholic group radicals determines the rate of etherification and the necessary quantity of that acid. The ease of etherification of the aliphatic alcohols increases from the primary to the secondary, and then to tertiary [1-5]. The presence of a phenyl radical or a styryl group at the carbon atom of the alcoholic group also facilitates the formation of the ethers. For example, triphenylcarbinol, benzhydrol, cinnamic and triphenylallylic alcohols etherify with great ease in the presence of small quantities and even traces of acids [6-16].

The etherification reaction of alcohols, with the use of sulfuric acid, is usually accompanied by their dehydration reactions with the formation of alkenes. The secondary process often sets the limit of feasibility of the use of the acid method for the production of ethers from alcohols which readily split off water. This pertains especially to unsaturated tertiary alcohols obtained from organomagnesium compounds and mesityl oxide. For these alcohols a very easy liberation of water and the formation of diene hydrocarbons are observed [17-21]. The reaction proceeds even in the presence of traces of organic acids or on heating, and strongly impedes the recovery of the alcohols themselves in the pure form. Moreover, we found that these same alcohols also very readily form ethers. Their etherification takes place at room temperature in the presence of small quantities of dilute sulfuric acid. A characteristic feature of the unsaturated alcohols which we studied is the presence in their molecule of a double bond in the allylic position to the alcoholic group. Such a combination of functional groups in the alcohol molecules was found to be extremely favorable for their etherification by the acid method.

Four unsaturated ethers which we obtained are described in the present report (Table).

Compound	Formula	Boiling point at pressure (mm) of	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Yield (in %)
1		40° (7); 147-148 (734)	1.4513	0.8192	44.91	44.94	70
2		53.5 (7)	1.4307	0.8140	49.58	49.55	60
3		53-55 (7)	1.4430	0.8361	53.26	53.70	53.4
4		114-117 (14)	1.5554	0.9667	52.21	50.57	91.3

The etherification of methylstyrylcarbinol took place much more difficultly than did the tertiary alcohols, and therefore required more acid. The discrepancy of the molecular refraction values, calculated and found for the four ethers, is undoubtedly accounted for by the presence of the conjugated double bonds of the benzene ring and of the side chain. It is necessary to note that we were unable to obtain ethers from allyl alcohol by this method.

EXPERIMENTAL

2,4-Dimethyl-4-methoxyhexene-2. 5 ml of an aqueous solution of sulfuric acid (1:5) was added to a solution of 8.5 g of 2,4-dimethylhexen-2-ol-4 in 20 ml of methyl alcohol. The mixture, at first homogeneous, after 3-5 minutes warmed up (25-27°), then rapidly became turbid and divided into two clear layers. The upper layer contained the ether, and the lower contained an aqueous solution of methyl alcohol and sulfuric acid. After addition of water, the upper layer was separated, dried with $MgSO_4$ and vacuum distilled. 6.6 g of the ether was obtained. It was a highly mobile liquid, and had a pleasant ethereal odor (physical constants are cited in the table).

Found %: C 76.36; H 12.72. M 146. $C_9H_{18}O$. Calculated %: C 76.05; H 12.67. M 142. Contained no active hydrogen

2,4-Dimethyl-4-ethoxyhexene-2. 7 ml of an aqueous solution of sulfuric acid (1:5) was added to a solution of 15 g of 2,4-dimethylhexen-2-ol 4 in 30 ml of ethyl alcohol. The reaction proceeded just as in the first instance. 11 g of the substance was obtained by distillation. It was a mobile liquid, which contained no active hydrogen (see table).

Found %: C 77.26; H 12.54 M 143.9, 145.7. $C_{10}H_{20}O$. Calculated %: C 76.92; H 12.70. M 156.

2,4-Dimethyl-4-allyloxyhexene-2. 5 ml of H_2SO_4 (1:5) was added to a solution of 10 g of 2,4-dimethylhexen-2-ol-4 and 15 g of allyl alcohol. A warming up of the mixture to 30° resulted. The reaction products were treated as in the preceding instances. 7 g of the ether, which was a colorless, mobile liquid, was obtained by distillation (see table).

Found %: C 78.63; H 12.18. M 161. $C_{11}H_{20}O$. Calculated %: C 78.53; H 11.99. M 168.

1-Phenyl-3-methoxybutene-1. 16 ml of 33% H_2SO_4 was added to a solution of 9 g of methylstyrylcarbinol in 18 ml of methyl alcohol. The reaction took place as in the preceding experiments. 10.4 g of a mobile, barely yellowish liquid, which contained no active hydrogen, was obtained by distillation (table).

Found %: C 80.91; H 8.74. M 168. $C_{11}H_{14}O$. Calculated %: C 81.48; H 8.62. M 162.

SUMMARY

Four unsaturated ethers were obtained by the action of dilute sulfuric acid on a mixture of the corresponding unsaturated alcohols with an allyl position double bond, and methyl, ethyl and allyl alcohols.

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PROBLEM OF THE DIRECTION OF REACTION OF SOME UNSATURATED HALIDE DERIVATIVES WITH ALCOHOLIC ALKALI

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By the action of alcoholic alkali on halogen derivatives, as is known, two reactions may occur; the nucleophilic replacement of halide by the alkoxy group, or the splitting off of hydrogen halide. The ratio between the rates of these two processes depends on the nature and structure of the halide derivatives and on the conditions of carrying out the reactions. A large number of works [1] has been devoted to the study of the mechanism of the nucleophilic replacement and the elimination of halogen.

Allyl type halide derivatives, upon addition of alcoholic alkalis, usually enter only into an exchange reaction. However, it was shown in one of the reports published earlier by the author, that upon the action of alcoholic KOH, 1,4-dibromobutadiene-1,2, unlike the other allyl halide derivatives, formed no ether due to the allylic bromine, but split off hydrogen bromide and gave, all things considered, vinylacetylene [2].

It is of interest to compare these data with the behavior of the simplest halide derivative of the present type, namely, 4-chlorobutadiene-1,2, under similar conditions.

The experiments which we set up showed that 4-chlorobutadiene-1,2, by the action of 2 N alcoholic KOH, split off hydrogen chloride vigorously and almost quantitatively, with the formation of vinylacetylene, i. e., as did 1,4-dibromobutadiene-1,2 itself. This observation corresponded to a brief specification in one of Carothers' patents [3].

In order to find the reasons for the unusual behavior of allyl halide derivatives of the $CH_2=C=CH-CH_2Hal$ type, we investigated the behavior of the three following primary chlorides, n-butyl chloride, crotyl chloride and 4-chlorobutene-1, toward alcoholic alkali under the same conditions.

Butyl chloride reacted very slowly, chiefly with the formation of ethyl butyl ether. Crotyl chloride reacted very vigorously, almost exclusively with the formation of ethyl crotyl ether. The yield of bivinyl was less than 1%. With respect to rate of reaction with the alkali, 4-chlorobutene-1 occupied a middle position, compared with the preceding chlorides, yielding chiefly bivinyl. The quantity of the ether which formed simultaneously did not exceed 2.5%.

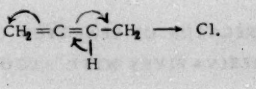
These differences in the behavior of the four chlorides can be accounted for on the basis of the theory of electronic displacement. Butyl chloride reacted slowly and in the direction of an exchange of the chlorine atom, since here only the inductive effect of the chlorine atom promoted the splitting off of chlorine and hydrogen. This effect led to the ionization of the carbon and chlorine bond and had little effect on the ionization of the hydrogen atoms attached to the adjacent carbon atom. The crotyl chloride vigorously replaced chlorine by alkoxyl, since the mobility of the chlorine atom here increases because of the conjugation of the C–Cl bond with the double bond. As a result of the conjugation, the double bond also increases the mobility of the hydrogen in the 4-position; however, it is obviously inadequate for bringing about the preferable 1,4-cleavage of the hydrogen halide:

$$H-CH_2-CH=CH-CH_2 \longrightarrow Cl.$$

The mobility of the chlorine atom in 4-chlorobutene-1 is less than that characterizing it in butyl chloride. However, the mobility of the hydrogen atom here is sharply increased under the influence of the two electron-gaining groups (double bond, CH_2Cl group). As a result of this double influence, the splitting off of hydrogen halide was the main direction of the reaction in this instance.

$$CH_2=CH-\underset{H}{CH}-CH_2 \longrightarrow Cl.$$

In the 4-chlorobutadiene-1,2 molecule with conjugated double bonds, both of the bonds (hydrogen and chlorine with carbon) interested us. The extraordinary ease of the splitting off of hydrogen halide was a consequence of this double conjugation:



The presence of the indicated effects in the chloride molecules considered was confirmed by the experimental values of the dipole moments for two of these substances. The dipole moment of 4-chlorobutadiene-1,2 (2.02 D) was lower than that for butyl chloride (2.07 D) [7]. This decrease of the dipole moment value can be explained by an electronic displacement due to the double bond toward the side opposite the shift, caused by the chlorine atom. Such a shift must bring about a protonization of the hydrogen atoms in the center of the molecule, which actually was observed.

However, it is necessary to observe that in a number of instances the chlorine atom may be replaced by the action of neutral or slightly alkaline reagents, for example, 4-chlorobutadiene-1,2. To such reagents belong solutions of Na_2CO_3, CH_3COONa, KCN, KBr, KI, NH_3 and other substances [4, 5]. In some cases the substituent also enters at another place in the molecule, for example, in the reaction with organomagnesium compounds [6].

From this it follows that the effect in the present case, to a considerable degree, has a dynamic character, and the polarization represented by the schemes is connected with the polarizing action of the reagent; in our case, hydroxyl or alkoxyl ions.

In reactions of some other unsaturated halide derivatives with alcoholic alkali, as shown earlier, the theory of electronic displacement also enabled us to explain satisfactorily the experimentally observed regularities [8].

EXPERIMENTAL

The butyl chloride used was commercial with a b. p. of 77-78°, d_4^{20} 0.8861 and n_D^{20} 1.4020. The crotyl chloride was obtained by the addition of hydrogen chloride to bivinyl in the presence of ferric chloride in glacial acetic acid [9]. Its b. p. was 81-83°, d_4^{20} 0.9266, n_D^{20} 1.4362. 4-Chlorobutene-1 was prepared by the action of phosphorus trichloride on allylcarbinol in the presence of pyridine [10]. Its yield amounted to 60%. Its b. p. was 76°, d_4^{20} 0.9207, n_D^{20} 1.4250. 4-Chlorobutadiene-1,2 had a b. p. of 87-88°, d_4^{20} 0.9876, n_D^{20} 1.4778.* The constants of the starting materials cited agree well with those indicated in the literature [9-11].

The action of alcoholic alkali on all of these chloro-derivatives was studied under the following conditions. A three-necked flask with a dropping funnel, reflux condenser and a small tube with rubber hose and clamp (for blowing through the apparatus), attached in sections, served as the reactor. At the end of the reflux condenser, in a section, a gas vent tube was attached, the other end of which was connected to an absorption bottle filled with a chloroform solution of bromine.

In all the experiments about 75 ml of a 2N alcoholic solution of KOH (one and one-half excess) was poured into the flask, after which it was heated to boiling of the alcohol, and then the chloride (0.1 mole) was introduced from the dropping funnel. After boiling the mixture for 1 hour, it was diluted twice with water and was again boiled for 1/2 hour in order to remove the hydrocarbon. Then the system was carefully blown out with air. The bromides of the unsaturated hydrocarbons were separated from the excess bromine (by means of a Na_2SO_3 solution) and from the chloroform (by vacuum distillation until the beginning of distillation of the corresponding bromide). The residue was weighed. The ethers were separated from the reaction mixture by distillation with water and with alcohol. The distillate was diluted with a $CaCl_2$ solution, washed with a solution of the same, dried over $CaCl_2$ and distilled. In the reaction flask, chloride-ion was determined (according to Volhard).

Butyl chloride. 0.746 g of chloride-ion was found, which corresponded to an extent of conversion of 21%. 8.0 g of a mixture of unreacted butyl chloride, and ethyl butyl ether with a b. p. of 77-83°, d_4^{20} 0.8470, n_D^{20} 1.3968 was obtained.

Found %: Cl 29.33, 30.07. C_4H_9Cl. Calculated %: Cl 38.30.

The analytical data indicated that the mixture contained about 23% of the ether. The ether yield was 17.3%, or 82% of the theoretical, considering the extent of conversion.

* The author expresses his appreciation to I. M. Dolgopolsky for submitting this preparation.

A total of 0.2 g of dibromobutane with n_D^{20} 1.5180 was isolated from the bottle containing the bromine solution. For 1,2-dibromobutane, in the literature n_D^{20} 1.5171 was cited [12]. The yield of the dibromide was less than 1%, or 5% of the theoretical.

Crotyl chloride. 3.52 g of chloride-ion was found. The extent of conversion was 99.2%. 7.8 g of ethyl crotyl ether was obtained. The yield was 78%.

B. p. 99-100.5°, d_4^{20} 0.7865, n_D^{20} 1.4050. Literature values [13]: b. p. 99-100°, d_4^{20} 0.7870, n_D^{20} 1.4050.

From the bottle with bromine 0.3 g of crystalline bivinyl tetrabromide was isolated. The yield was less than 1%.

4-Chlorobutene-1. 2.89 g of chloride-ion was found. The extent of conversion was 81.5%. A total of 0.6 g of a mixture of unreacted chlorobutene and the ether was obtained.

B. p. 83-90°, d_4^{20} 0.8417, n_D^{20} 1.4080.

Found %: Cl 16.08. C_4H_7Cl. Calculated %: Cl 39.16.

The analytical data indicated that the mixture contained about 41% of unreacted chloride. Hence, the ether yield was less than 2.5%.

From the absorption bottle, 27.8 g of crystalline bivinyl tetrabromide was isolated. The yield was 75%, or 92% of the theoretical, considering the extent of conversion.

4-Chlorobutadiene-1,2. 3.41 g of chloride-ion was found. The extent of conversion was 96%. No ether was isolated. The yield of the bromides amounted to 26.5 g, or 73% by calculation for vinylacetylene tetrabromide.

B. p. 123-125° (8 mm), n_D^{20} 1.6300.

Found %: Br 86.80, 86.47. $C_4H_4Br_4$. Calculated %: Br 86.00.

SUMMARY

1. The direction of the reaction of the four chlorides, butyl chloride, crotyl chloride, 4-chlorobutene-1 and 4-chlorobutadiene-1,2 with 2 N alcoholic KOH, was investigated.

2. It was shown that the first two chlorides gave mainly the corresponding ethers, whereas the last two chiefly split off hydrogen chloride, forming bivinyl and vinylacetylene, respectively.

3. An explanation of the regularity found was given on the basis of the theory of electronic displacement.

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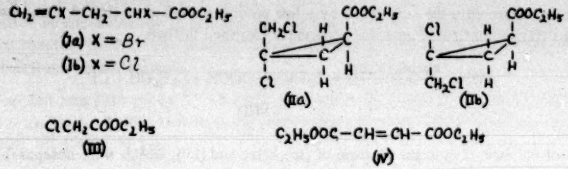
REACTIONS OF ALIPHATIC DIAZO-COMPOUNDS WITH UNSATURATED COMPOUNDS

XIX. REACTION OF ETHYL DIAZOACETATE WITH 2,3-DICHLOROPROPENE IN THE PRESENCE OF CUPRIC SULFATE

I. A. Dyakonov and T. V. Domareva

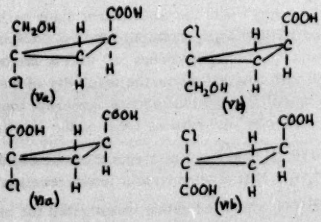
The ester (Ia) was obtained as the sole product of the reaction between ethyl diazoacetate and 2,3-dibromopropene in the presence of cupric sulfate [1]. It was found in the present work that an analogous reaction with 2,3-dibromopropene led to the formation of a mixture of different esters: (Ib), 27.6%; (IIa), 42.9%; (IIb), 20.8%; (III), 2.7%; and (IV), 5.9% (total weights of all the esters = 100%).



The low-boiling ester (III) was isolated by direct distillation of the mixture and was converted to the amide (IIIa) for proof:

$$(III) \xrightarrow[C_2H_5OH]{NH_3} ClCH_2CONH_2. \quad (IIIa)$$

The separation of esters (Ib), (IIa), (IIb) and (IV) was difficult because of the close boiling points of these substances. We were able to isolate only the cyclic esters (IIa) and (IIb) by treatment of the whole mixture with a cold permanganate solution. Both stereoisomers were isolated in analytically pure form, but because of the proximity of the boiling points, the possibility that each of them contained a small impurity of the other was not excluded. Both stereoisomers had different physical constants (d_4^{20}, n_D^{20}), and the non-identical hydroxy acids, (Va) with a m. p. of 106-107°, and (Vb) with a m. p. of 108-109°, (the non-identity was determined by a mixed sample) were obtained by alkaline hydrolysis of the stereoisomers. Moreover, as a result of the alkaline hydrolysis and of a subsequent oxidation, two dicarboxylic acids, which differed as to melting points, were obtained in the aqueous solutions – (VIa) with a m. p. of 156-157° and (VIb) with a m. p. of 194-195°.



The cis-configuration was attributed to the acids (Va) and (VIa) with lower melting points, which were obtained from the low-boiling ester (IIa), but the trans-configuration was attributed to the high-melting (Vb) and(VIb), which were obtained from the high-boiling ester (IIb). In accordance with this, the stereoisomeric configurations for the esters themselves were represented. The cyclic structure of (IIa) and (IIb) was determined completely by the transformations indicated here.

In order to establish the presence of (Ib) in the mixture, its permanganate-oxidation products were analyzed after the separation of (IIa) and (IIb). As a result of the precise oxidation, we were able to isolate the ester (VII) in one of the experiments. The catalytic dehalogenation of the crude preparation (VII) [possible admixture of oxalic acid (VIII)] led to the formation of succinic acid (IX).

$$\text{(Ib)} \xrightarrow{KMnO_4} CO_2 + HOOC-CH_2-CHCl-COOC_2H_5 + Cl',$$

(VII)

$$\text{(VII)} \xrightarrow{H_2(Pd/CaCO_3),\ NaOH} HOOC-CH_2-CH_2-COOH. \qquad \text{(IX)}$$

The acid (IX) could be formed only by the dehalogenation of (VII), which also showed the presence of (Ib) in the mixture investigated. For a quantitative determination of (Ib), the content of chlorine which mineralized as a result of the oxidation was determined. (The appearance of Cl-ion in the solution could be brought about only by the oxidation of (Ib), since (IIa) and (IIb) were not oxidized under these conditions).

We were able to isolate only the acid (VIII) by a less precise oxidation of (Ib) in a mixture with (IIb). Under these conditions the (VII) which first formed was apparently oxidized further:

$$\text{(VII)} \xrightarrow{KMnO_4(KOH)} 2HOOC-COOH + C_2H_5OH + Cl'.$$

(VIII)

The presence of the ester (IV) in the mixture of (Ib), (IIa) and (IV), which were unseparable by distillation, can be determined by the results of an analysis of this mixture: the chlorine content proved to be reduced but the ethoxyl content was elevated, compared with those calculated for the formula of (Ib) or (IIa). The quantitative content of (IV) in the mixture was calculated from these data, and also from a consideration of the content of the isomers (Ib) and (IIa), which was determined by a different method (see above). Both methods of calculation led to similar results.

Comparing the data of this investigation with those which were obtained earlier on carrying out the reaction between ethyl diazoacetate and allyl chloride [2], it can be concluded that to a certain extent in both instances the reactions proceed analogously. The main difference consisted only in that the cyclic ester [sum of (IIa) and (IIb)], but not the linear (Ib), formed in appreciably high yield in the reaction with 2,3-dichloropropene, whereas a reverse relationship of the yields of the cyclic and linear isomers was observed in the reaction with allyl chloride.

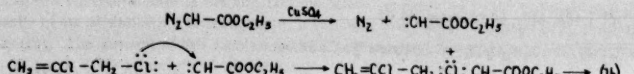
This difference could be accounted for by the fact that, because of the presence of chlorine at the double bond in the 2,3-dichloropropene: 1) the additive capacity of the double bond increased, as compared with the allyl chloride; and 2) the mobility of the allyl chlorine decreased in comparison. Since the reactions leading to the formation of cyclic and linear isomers are competitive (in both cases), each of these hypotheses taken separately could explain the simultaneous increase of the yield of isomers (IIa) and (IIb) and the decrease of the yield of isomer (Ib) in the reaction with 2,3-dichloropropene.

However, the first hypothesis did not agree with the observations made earlier of the relative reactivities of some bromo-derivatives: the addition of $\rangle CHCOOC_2H_5$ radical to the $\rangle C=C\langle$ bond also did not occur in the reaction of ethyl diazoacetate with 2,3- and 1,3-dibromopropenes or with α-bromoallylacetate. The second hypothesis was more likely. It not only agreed with observations on the reactivity of the corresponding bromo-derivatives (the yield of linear isomer in the reaction with 2,3-dibromopropene was lower than in the reaction with allyl bromide [1, 3]), but could also be brought into conformity with existing ideas on the reaction mechanism [4, 5].

As one of us has already indicated [6, 7], electrophilic rather than nucleophilic properties should be attributed to the free carbethoxycarbene $CHCOOC_2H_5$.* If it is assumed that in this reaction also it is the reagent which acts

* In D. Phillips' recently published work [8], where the author investigated the mechanism of the reaction of ethyl diazoacetate with allyl halides, which we described, there was a statement of the possibility of the combination of both electrophilic and nucleophilic properties in the free carbethoxycarbene.

[9], then electrophilic attack on the allyl halide atom (cf. [4]) will take place more successfully the more readily the latter will yield its electrons to a foreign atomic nucleus:



The presence of chlorine at the double bond, which has an I-effect, will prevent the transfer of electrons to the free carbethoxycarbene, and also to the individual organic cation $CH_2=CCl-CH_2^+$ from (X) in the second stage of the reaction. Therefore, the capacity for the formation of a linear isomer must be less for the reaction with 2,3-dichloropropene than for the reaction with allyl chloride.

EXPERIMENTAL

Starting materials: 1) the 2,3-dichloropropene had a b. p. of 94-95°, d_4^{20} 1.212, n_D^{20} 1.461 [10]; 2) ethyl diazoacetate was not purified by vacuum steam-distillation [11]; 3) the catalyst was anhydrous cupric sulfate.

1. Condensation. A solution of 160 g (1.4 moles) of ethyl diazoacetate in 200 g of 2,3-dichloropropene (total quantity of the dichloropropene was 480 g, 4.3 moles) was added slowly (during 6-7 hours), with stirring, to 280 g of 2,3-dichloropropene and 1.8 g of cupric sulfate, heated at about 70-80°. Just as described earlier also [1-3], the reaction was accompanied by the evolution of nitrogen (31.4 liters at 17.5° and 755.3 mm, or 93.6%). On completion of the experiment the reaction product was cooled, filtered off from the catalyst and fractionated in vacuo; moreover, the following fractions were obtained:

Fr. 1. 45-50° at 182 mm (310 g); Fr. 2. 47.5-49° at 14 mm, n_D^{17} 1.4230 (3.1 g); Fr. 3. 49° at 14 mm – 72° at 3 mm, n_D^{17} 1.4410 (9.0 g); Fr. 4. 72-78° at 3 mm, n_D^{17} 1.462 (84.4 g); Fr. 5. 78-85° at 3 mm, n_D^{17} 1.464 (15.2 g); Fr. 6. 85-94° at 3 mm, n_D^{17} 1.469 (30.9 g).

The 1st fraction was regenerated 2,3-dichloropropene (2.8 moles). The 2nd fraction was assumed to be the ester (III) on the basis of a comparison of its constants with the literature values (m. p. 52° at 20 mm, n_D^{20} 1.422) and on the basis of production of the chloroacetamide from it, by the action of a 20% solution of ammonia [2]. Its m. p. was 119-120°. It was identified in a mixed melting test with known chloroacetamide. The 3rd fraction, as the intermediate, was not studied. In the 4th fraction, the chlorine content was found to be reduced, but the ethoxyl content was elevated, compared with those calculated for the esters (Ib) or (IIa) of the general formula $(C_5H_5OCl_2)OC_2H_5$:

d_4^{20} 1.192, n_D^{20} 1.462.

Found %: Cl 31.25, 31.14; OC_2H_5 25.6. M 177.5, 182.7. $(C_5H_5OCl_2)OC_2H_5$. Calculated %: Cl 36.04; OC_2H_5 25.6. M 197.1.

A discrepancy resulted due to an impurity of the ester of fumaric acid. On the basis of the results of a further investigation (see 2a and 2b), it was found that the 4th fraction was a mixture of the three esters, which were difficultly separable from each other by distillation: (IIa), (Ib) and (IV). The 5th fraction was not investigated, as it was intermediate (judging by the index of refraction, it, apparently, was close in composition to the 4th fraction). An analysis of the 6th fraction showed that the chlorine content and the molecular weight of the substance of this fraction were close to those calculated for the formula $(C_5H_5OCl_2)OC_2H_5$.

Found %: Cl 36.59. M 188.4, 190.9. $C_7H_{10}O_2Cl_2$. Calculated %: Cl 36.04. M 197.1.

As a result of a subsequent oxidation, it was found that the 6th fraction consisted essentially of (IIb) with a small admixture of (Ib) (see below).

2. Investigation of the 4th fraction. a) Ethyl ester of cis-2-(chloromethyl)-2-chlorocyclopropane-1-carboxylic acid (IIa). Potassium permanganate was added gradually, with shaking, to 84.4 g of the substance of the 4th fraction and 42 ml of water, cooled to 0°, until the appearance (in the cold) of a violet color of the solution. On the whole, 90.8 g of $KMnO_4$ was consumed. The excess of oxidizing agent was removed by addition of thiosulfate, and the colorless solution, together with the cyclic ester oil (IIa) which remained, was filtered off from the manganese dioxide. The ester was extracted with ethyl ether, and the ether extracts were combined with those separated from the aqueous layer (IIa). The aqueous layer also was extracted with ether, and the combined ether extracts were dried with

anhydrous sodium sulfate. After removal of the ether, the residue was vacuum distilled. The distillate was a colorless oil with a b. p. of 72-73° at 2 mm. The yield of (IIa) with the specified boiling point was 48.7 g (17.6% by calculation on the basis of the initial ethyl diazoacetate).

d_4^{20} 1.234, n_D^{20} 1.469, MR_D 44.45; calc. 44.42.

Found %: Cl 35.78. $C_7H_{10}O_2Cl_2$. Calculated %: Cl 36.04.

b) The ester of α, γ-dichloroallylacetic acid (Ib). (Determination of its content in the 4th fraction). The aqueous solution of the oxidation products, separated from the ester (IIa), was brought to a volume of 500 ml. 4 samples of 25 ml each were withdrawn from the solution. A determination of chloride-ion in the first two samples were made volumetrically (according to Mohr). On conversion to the weight of the remaining solution, moreover, chloride-ion was found (in g) to be 5.24 and 5.31. The remaining two samples of solution were acidified with nitric acid, and were heated with a solution of silver nitrate for 2 hours. As a result, the following values for the chloride-ion content in the solution after boiling were obtained (in g): 11.53 and 11.71. The quantity of (Ib) removed from the 4th fraction by oxidation could be calculated, proceeding from the chloride-ion content in the aqueous solution, which was determined by the methods indicated here (see Introduction). The quantity of (Ib), calculated by the first method (without heating), was equal to 29.3 g, but by the second method it was equal to 32.3 g, or to 10.6 and 11.7%, respectively, on the basis of the initial ethyl diazoacetate.

The aqueous solution which remained after withdrawal of the samples was acidified to Congo with sulfuric acid, and was subjected to further prolonged ether extraction in a percolator. From the ether extract, 13 g of a partially crystallizing oil was obtained, which was assumed to be the crude ester (VII).

Found %: Cl 18.37. $C_6H_9O_4Cl$. Calculated %: Cl 19.63.

The contamination of the preparation might be due to an admixture of the acid (VIII) (or its acid ester), which formed as a result of the more thorough oxidation of (VII) (see Introduction), or might be due to the oxidation of (IV).

For a definite identification of the crude ester (VII), it was converted to the acid (IX) by dehalogenation followed by hydrolysis: 3 g of (VII), 40 ml of alcohol, 12 ml of 10% alcoholic solution of potassium hydroxide and 13 g of 1% $Pd/CaCO_3$ were saturated with hydrogen, with mechanical stirring, in a hydrogenation apparatus. 272 ml of H_2 (0°, 760 mm) was absorbed, which amounted to 78.8% of the calculated quantity. After removal of the catalyst the solution was heated with 5 g of sodium hydroxide on the water bath for 30 minutes, neutralized with dilute sulfuric acid, and the ethyl alcohol was steam-distilled. The remaining aqueous solution was acidified to Congo with sulfuric acid and was extracted in the percolator. 1.5 g (76.5%) of the acid (IX), with a m. p. of 180-181° (from water), was isolated from the ether extract.

Found: equiv. 59.8. $C_2H_4(COOH)_2$. Calculated: equiv. 59.2.

The acid was identified by a mixed melting test with known succinic acid.

c) Diethyl fumarate (IV) (determination of its content in the 4th fraction). The calculation of the content of (IV) was made by two methods, namely: by a comparison of the percent of ethoxyl found in the 4th fraction with that calculated for the pure esters (Ib) and (IV), and by the difference of the weight of the 4th fraction (84.4 g) and the sum of the weights of (IIa) and (Ib) (48.7 g + 29.3 g). By the first method the content of ester (IV) was 6.7 g, but by the second it was 6.4 g, i. e., 8.0 and 7.8% by weight of the 4th fraction, respectively.

3. Investigation of the 6th fraction: ethyl ester of trans-2-chloromethyl-2-chlorocyclopropane-1-carboxylic acid (IIb). Pulverized potassium permanganate was added to 30.9 g of the substance of the 6th fraction and 200 ml of water, without external cooling (cf. 2a), until the appearance of a violet color. In order to remove the color, the solution was heated on the water bath. In all, 4.6 g of $KMnO_4$ was consumed. After a treatment similar to that described in (2a), 23.6 g (8.5%) of the analytically pure ester (IIb), with a b. p. of 98-99° at 5 mm, was isolated.

d_4^{20} 1.244, n_D^{20} 1.473, MR_D 44.45; calc. 44.42.

Found %: Cl 36.20. $C_7H_{10}O_2Cl_2$. Calculated %: Cl 36.04.

The aqueous solution of the oxidation products, separated from (IIb), was acidified to Congo with dilute sulfuric acid, and was extracted with ether in the percolator. 2 g of (VIII), with a m. p. of 96-98°, was isolated from the ether extract. After crystallization from water, its m. p. was 100-101°. A mixed test with the known dihydrate, $(COOH)_2 \cdot 2H_2O$, melted without a depression. The results of a determination of the equivalent of (VIII) and of an analysis of its calcium salt are cited below.

Found: equiv. 62.17, 64.25. $(COOH)_2 \cdot 2H_2O$. Calculated: equiv. 63.02.

Found %: Ca 27.46. $Ca(COO)_2 \cdot H_2O$. Calculated %: Ca 27.43.

Considering the analytical date of the 6th fraction, which corresponded to the composition $C_7H_{10}O_2Cl_2$, and considering the results of its oxidation by permanganate, it followed that, besides the ester (IIb), it contained an admixture of the ester (Ib). The amount of this admixture could be evaluated approximately from the consumption of permanganate: 2.1 g or 6.8% by weight of the fraction.

4. Cis-2-(hydroxymethyl)-2-chlorocyclopropane-1-carboxylic acid (Va). 5 g of the ester (IIa) and 300 ml of a 10% solution of soda were boiled, with mechanical stirring, until there was complete dissolution of the ester layer. The cooled solution was neutralized with dilute sulfuric acid, and the alcohol which formed during the hydrolysis was steam-distilled. The solution which remained in the distillation flask was concentrated on the water bath, acidified with 50% H_2SO_4, with cooling, and (Va) was extracted from the solution with ether in the percolator. After removal of the ether 1.7 g (44.5%) of the crude (Va), with a m. p. of 94-95°, was obtained. A double crystallization from a mixture of benzene and acetone increased the melting point to 106-107°. Its yield was 0.9 g (23.6%).

Found %: Cl 23.29, 23.17. Equiv. 151.2, 150.7. $(C_4H_9OCl)COOH$. Calculated %: Cl 23.55. Equiv. 150.6.

(Va) consisted of colorless, coarse crystals, which were highly soluble in water, acetone and ether, but were more difficultly soluble in benzene.

5. Cis-1-chlorocyclopropane-1,2-dicarboxylic acid (VIa). 10 g of the ester (IIa) was hydrolyzed with a 10% solution of soda under the conditions described above. After neutralization of the excess soda and after removal of the alcohol, potassium permanganate was added to the resulting solution of the salt of (VIa). The oxidation was carried out in the cold, but later with heating on the water bath. 18 g of $KMnO_4$ in all was consumed. After the usual treatment, the solution of the oxidation products was acidified with sulfuric acid and was extracted with ether in the percolator. 1.8 g of crude (VIa), with a m. p. of 124-132°, was obtained from the ether extract. After two crystallizations from a mixture of benzene and acetone, (VIa) had a constant m. p. of 156-157°. The solubility of (VIa) in water and in organic solvents was the same as for (Va).

Found %: Cl 21.45. $C_5H_5O_4Cl$. Calculated %: Cl 21.56.

6. Trans-2-(hydroxymethyl)-2-chlorocyclopropane-1-carboxylic acid (Vb). As a result of the hydrolysis of 5 g of the ester (IIb) with a 10% solution of soda (11.2 g), and a subsequent treatment of the solution as indicated in Section 4, 0.5 g of (Vb) with a m. p. of 108-109° (from a mixture of benzene and acetone) was isolated. A mixed sample with the cis-acid (Va, m. p. 106-107°) melted 16° lower than did this acid.

Found %: Cl 23.56, 23.28. $C_5H_7O_3Cl$. Calculated %: Cl 23.55.

7. Trans-2-chlorocyclopropane-1,2-dicarboxylic acid (VIb). This acid was obtained analogously to (VIa), by the hydrolysis of 6 g of the ester (IIb) with a 10% solution of soda (13.5 g), followed by treatment of the resulting solution of the salt of (Vb) with potassium permanganate (13.5 g). The isolation of (VIb) from the solution was carried out just as in Section 5. The yield was 0.8 g, with a m. p. of 191-192.5°. The m. p. was 194-195° after crystallization from a mixture of benzene and acetone. Its solubility in water and in organic solvents was the same as for (VIa).

Found %: Cl 21.43. $C_5H_5O_4Cl$. Calculated %: Cl 21.56.

SUMMARY

As a result of the reaction of ethyl diazoacetate with 2,3-dichloropropene, in the presence of cupric sulfate, a mixture of the esters of chloroacetic, fumaric, α, γ-dichloroallylacetic and cis- and trans-2-chloro-2-(chloromethyl)-chloropropane-1-carboxylic acids was obtained, in percentage relationships of 2.7, 5.9, 27.6, 42.9 and 20.8, respectively. An alkaline hydrolysis of the stereoisomeric esters led to the formation of cis- and trans-2-chloro-2-methylolcyclopropane-1-carboxylic acids, and a subsequent oxidation led to the formation of cis- and trans-2-chlorocyclopropane-1,2-dicarboxylic acids. None of the stereoisomers obtained in this work was described in the literature. The results of the present investigation were in agreement with the results of the preceding works [1-3] and with existing ideas on the mechanism of reactions of this type [4, 5].

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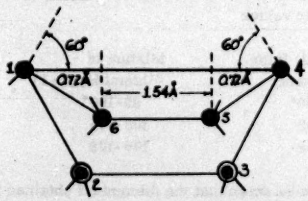
INVESTIGATIONS IN THE FIELD OF UNSATURATED CYCLIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

XVIII. SYNTHESIS AND STUDY OF 1,4-DIBROMOCYCLOHEXENE-2

N. A. Domnin, N. S. Shutova and K. M. Belyaeva

In 1903 N. D. Zelinsky and S. S. Nametkin [1], then in 1927 N. D. Zelinsky and K. A. Kocheshkov [2], made attempts to synthesize bicyclo-0,2,2-hexane. On the basis of the works carried out, these investigators concluded that they obtained bicyclo-0,2,2-hexane. However, the authors gave no well-defined and reliable evidence in favor of its structure. Moreover, it can be confirmed that from the stereochemical point of view the capacity for the existence of this bicyclic hydrocarbon is not very likely, since its molecule must be extremely deformed. As the figure presented shows, the formation of a bridge in the 1,4-position in the cyclohexane is connected with a bending of the two valence angles through at least 50-60°, and besides, the chemical bond which forms a bridge between the 1,4-carbon atoms, is probably stretched from its normal value of 1.54 A to (0.72 + 1.54 + 0.72) 2.98 A, if we proceed from the mobile (tub-form) form of cyclohexane.

In connection with the considerations expressed, the problem of the ability of bicyclo-0,2,2-hexane to exist is of much interest and must be subjected to further experimental investigation.



It was necessary to obtain 1,4-dibromocyclohexane as the starting material for the synthesis of bicyclo-0,2,2-hexane. For this purpose we proposed to obtain 1,4-dibromocyclohexene-2 by the action of molecular bromine on cyclohexadiene-1,3, and then to obtain 1,4-dibromocyclohexane via its hydrogenation.

We continued work in this direction. However, independently of its results, we assumed it expedient first to report some interesting data on 1,4-dibromocyclohexene-2. Earlier, we carried out investigations devoted to this dibromide [3]. In this work we were able to obtain dibromocyclohexene with m. p. of 99-100, 103-104 and 107-108°. It is most likely that these three forms of the dibromide are isomorphic forms, since they form under different conditions and in some instances are converted into each other. However, keeping in mind that the six-membered ring may exist in many spatial forms, and in the presence of two substituents may give geometric, bipolar, biequatorial and polar-equatorial isomers, it is possible that the three forms of dibromocyclohexene which we obtained are also isomers of such a type. In any case, we demonstrated experimentally that the dibromocyclohexenes with similar melting points, but obtained by different methods, are identical. The problem of the isomerism of the six-membered ring derivatives is of great theoretical interest, and its study is essential and necessary.

EXPERIMENTAL

We carried out the synthesis of 1,4-dibromocyclohexene-2 with a m. p. of 99-100° by a method described earlier [3]. This dibromide, recrystallized from petroleum ether, formed a dibromide with a m. p. of 103-104°. On long standing of the mother liquor, a dibromide with a m. p. of 108-109° precipitated from it.

The properties of the dibromocyclohexene with a m. p. of 99-100° were

Found %: Br 66.45, 66.51. M 244, 237. $C_6H_8Br_2$. Calculated %: Br 66.66. M 240.

The dibromides with m. p. of 103-104 and 108-109° had the same molecular weight and the same bromine content.

In the work [3] we obtained substances with m. p. of 55-56, 66-68 and 90-93°; in molecular weight and bromine content they all corresponded to dibromocyclohexene.

We found that the resulting crude product of the bromination of cyclohexadiene-1,3, with a m. p. of 45-80°, after its recrystallization from alcohol gave a dibromide with a m. p. of 90-93°. However, in spite of numerous attempts to investigate these substances, we obtained no definite and well-defined results.

As Zigler [4], and Schmidt and Karrer [5], showed, the hydrogens in the α-position with respect to the double bond (allylic position) are readily replaced by bromine, if some N-halogen compound, for example, N-bromophthalimide and N-bromosuccinimide, is used as the brominating agent.

Cyclohexene with a m. p. of 83-84°, n_D^{22} 1.4449 was brominated by N-bromosuccinimide in boiling carbon tetrachloride, according to Zigler (32.5% yield of monobromocyclohexene), and according to Schmidt and Karrer, with benzoyl peroxide as the catalyst (51% yield of monobromocyclohexene).

The bromination of monobromocyclohexene to dibromocyclohexene was also carried out by Zigler (30% yield). The melting point of the crude crystalline substance obtained was 88-96°, and after drying, it was 94-95°. A portion of the resulting crystals was washed with alcohol in the cold. After drying on a watch glass, the crystals had the form of long, clear prisms, and a m. p. of 98-100°. All the crystal substance obtained was recrystallized from light petroleum ether (45-60° fraction). After hot filtration, the crystals precipitated as long needles. In the event of a slow crystallization, well-formed clear crystals of prismatic form were precipitated. Recrystallized from petroleum ether (45-60° fraction) a second time, the 1,4-dibromocyclohexene-2 had a m. p. of 107-108°.

Found %: Br 66.42, 66.48. M 236, 234. $C_6H_8Br_2$. Calculated %: Br 66.66. M 240.

The dibromide with a m. p. of 98-100° also corresponded to 1,4-dibromocyclohexene-2 in molecular weight and bromine content.

If we take the same dibromides and mixtures (1:1) of the dibromides obtained from cyclohexadiene-1,3 by the action of molecular bromine, and the dibromides obtained by the bromination of cyclohexene with N-bromosuccinimide, their melting points have the following characteristic values:

Dibromide from cyclohexadiene-1,3	Dibromide from cyclohexene	Mixture of dibromides (1:1)
99-100°	98-100°	99-100°
103-104	107-108	103-104
108-109	107-108	108-109

On the basis of the data obtained, the sound conclusion can be drawn that the dibromides obtained from cyclohexadiene-1,3 by the addition of molecular bromine to it, and the dibromides obtained from cyclohexene by its bromination with N-bromosuccinimide, were identical, which serves as an indirect verification of their structure.

We tried to carry out a direct and straightforward verification of the structure of the dibromides by their hydrogenation and oxidation.

No hydrogenation occurred at all over Raney nickel, but over a palladium catalyst a quantitative replacement of 2 bromine atoms by 2 hydrogen atoms took place.

The electrolytic hydrogenation of 1,4-dibromocyclohexene-2 was carried out in a dioxane solution with a copper cathode, with a coating of freshly-deposited nickel black [6]. However, as a result, 1,4-dibromocyclohexene-2 with a m. p. of 102-104° was recovered, which after recrystallization from petroleum ether (45-60° fraction) had a m. p. of 105-107°.

Oxidation by ozone and by potassium permanganate gave no positive results.

SUMMARY

1. It was found that dibromocyclohexene with a m. p. of 108-109°, which formed on addition of bromine to cyclohexadiene-1,3, was identical with the dibromocyclohexene with a m. p. of 107-108° which was obtained by the bromination of cyclohexene by N-bromosuccinimide.

2. It was found that dibromocyclohexene exists in three variants with m. p. of 99-100, 103-104 and 107-108° (108-109°) which, probably, are isomorphic forms.

3. It was shown that it is impossible to verify the structure of 1,4-dibromocyclohexene-2 by chemical methods.

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SYNTHESIS AND INVESTIGATION OF 1,2-DIPHENYL-1-α-AND 1-β-NAPHTHYL-2-BROMOETHYLENES

A. M. Khaletsky and A. Ya. Kaplan

In the preceding works it was shown by one of us and A. M. Yanovitskaya [1] that, by the action of bromine on the cyclohexyl derivatives of the aryl ethylenes, the replacement of hydrogen by bromine is closely connected with the nature of the radicals and of the substituting groups.

As investigation of the problem of the structural properties of the molecule, which affect the mechanism of the reaction of formation of the bromoarylethylenes, was extremely important, not only for information about the stability of the hydrogen bond of the ethylene group, but also for the synthesis of bromo-substituted ethylenes, because the latter affect the hormonal activity of the estrogens, and some of them are anticarcinogens.

As Schueller [2] showed, the estrogenic properties and their prolongation increased sharply with the replacement of hydrogen of the ethylene group of triphenylethylene by bromine; on the contrary, the replacement of the hydrogen of the aromatic nucleus by bromine reduced the activity [3].

Thus, the stability of the hydrogen at the double bond depends on the nature of the radicals and on the position of the substituent groups; electronegative groups stabilize the hydrogen-carbon bond of the ethylene group.

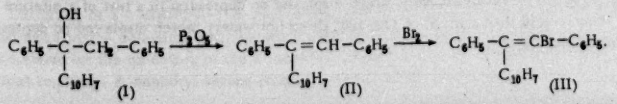
At present a sufficient number of bromoethylenes with phenyl and alkyl radicals has been described; however, only a single representative with naphthyl radicals was encountered in the literature. Moreover, they had significant interest for our purposes of the synthesis of hormonal substances. Thus, it was of interest to learn what the reactivity of the hydrogen on the ethylene bond carbon was in the replacement of phenyl by α- or β-naphthyl. It could be expected that such a replacement probably changes the mechanism of the bromination reaction essentially; the experimental data confirmed our assumption. Thus, 1,2-diphenyl-1-α-(or β-)-naphthyl-2-bromoethylenes were formed by the bromination of 1,2-diphenyl-α-(or β-)-naphthyl-2-ethylenes.

These compounds were synthesized from the isomeric phenyl-α- or β-naphthyl ketones, obtained by Lechner's method [4]. A number of other methods besides this method are described in the literature [5]. We used Rousset's method [6] for the separation of the isomeric ketones.

The ketones were introduced into the organomagnesium synthesis with benzyl chloride according to Bauer [7]; the yield of phenyl-α-naphthylbenzylcarbinol (I) reached 60%, when the reaction of benzyl chloride with magnesium proceeded to completion. Benzyl alcohol and bibenzyl formed simultaneously with phenyl-α-naphthylbenzylcarbinol.

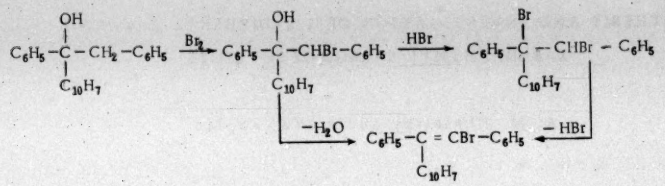
We were unable to carry out the dehydration of phenyl-α-naphthylbenzylcarbinol in an acetic acid or benzene medium in the presence of sulfuric acid, either by direct distillation or by distillation in the presence of anhydrous oxalic acid, or acetic anhydride. Only by heating in the presence of phosphoric anhydride, or potassium bisulfate or by passage of hydrogen chloride into a benzene solution of the carbinol (I), was the latter dehydrated, with the formation of 1,2-diphenyl-1-α-naphthylethylene (II). The structure of the unsaturated hydrocarbon was demonstrated by oxidation with potassium permanganate to phenyl α-naphthyl ketone and benzoic acid.

On bromination of 1,2-diphenyl-α-naphthylethylene with bromine in glacial acetic acid, a product with an extended melting point was obtained, which corresponded in bromine content to the formula $C_{24}H_{17}Br$. In order to demonstrate the structure of the latter, it was oxidized by potassium permanganate in the presence of sodium carbonate; moreover, phenyl α-naphthyl ketone and benzoic acid were formed and bromide-ion was determined as AgBr. All these products undoubtedly demonstrated the structure of 1,2-diphenyl-1-α-naphthyl-2-bromoethylene (III):



(I) (II) (III)

The bromination reaction (I) was investigated for the purpose of the synthesis of 1,2-diphenyl-1-α-naphthyl-2-bromoethylene (III) from phenyl-α-naphthylbenzylcarbinol (I). It can be assumed that this reaction takes place according to the scheme:



It was demonstrated experimentally that 1,2-diphenyl-1-α-naphthyl-2-bromoethylene actually formed on bromination of phenyl-α-naphthylbenzylcarbinol.

We carried out the synthesis of isomeric 1,2-diphenyl-1-β-naphthyl-2-bromoethylene from phenyl-β-naphthylbenzylcarbinol similarly to the preceding. 1,2-Diphenyl-1-β-naphthylethylene was formed by the dehydration of the carbinol, the structure of which also was demonstrated by oxidation by potassium permanganate (phenyl β-naphthyl ketone and benzoic acid formed).

1,2-Diphenyl-1-β-naphthyl-2-bromoethylene (m. p. 206-206.5°), with a yield of 54.4% with respect to the carbinol, was formed by the bromination of 1,2-diphenyl-1-β-naphthylethylene. Thus, in the present instance also, on replacement of the α-naphthyl by the β-naphthyl radical, the reaction took place entirely analogously.

Pharmacological investigations of the isomeric diphenylnaphthylbromoethylenes which we synthesized showed that they had a sufficiently high, prolonged estrogenic activity, taking second place, however, to syn-estrol (p,p-dihydroxy-3,4-diphenylhexane).

EXPERIMENTAL

Phenyl α- and β-naphthyl ketones were synthesized according to Lechner [4].

17.5 g (75.4% with respect to benzyl chloride) of a substance with a b. p. of 216-224° at 8 mm, which crystallized immediately, was obtained from 14 g of benzyl chloride, 26.5 g of naphthalene, and 0.4 g of phosphoric anhydride. We used Rousset's method [6] for the separation of the isomeric α- and β-phenyl naphthyl ketones; moreover, 9.8 g (56.9%) of phenyl α-naphthyl ketone with a m. p. of 75° (from alcohol) and 4.1 g (23.4%) of phenyl β-naphthyl ketone with a m. p. of 82° (from alcohol) were obtained.

Phenyl-α-naphthylbenzylcarbinol. It was obtained according to Bauer [7]; 25.5 g (60%) of phenyl-α-naphthylbenzylcarbinol with a m. p. of 148.5-151° (from alcohol), 5.5 g of benzyl alcohol with a b. p. of 205°, 8 g of bibenzyl with a m. p. of 50-52° and 15 g of a resinous residue were obtained from 4.8 g of magnesium turnings, 25.3 g of benzyl chloride in 150 ml of ether, and 30 g of phenyl α-naphthyl ketone in 120 ml of benzene.

Because Bauer [7] did not cite an analysis of the carbinol, we cite our analytical data below.

Found %: C 88.50, 88.50; H 5.99, 6.25; OH 5.32, 5.29. M 314.2, 319.1. $C_{24}H_{20}O$. Calculated %: C 88.88; H 6.21; OH 5.24. M 324.

1,2-Diphenyl-1-α-naphthylethylene. 1.5 g (79%) of a hydrocarbon was obtained by the dehydration of 2 g of phenyl-α-naphthylbenzylcarbinol in 40 ml of benzene, in the presence of 1 g of phosphoric anhydride at 80°. 1.5 g (63.15%) of a hydrocarbon was obtained by the dehydration of 2 g of the carbinol under similar conditions in the presence of potassium bisulfate; lower yields were obtained by the dehydration in the presence of hydrogen chloride.

Found %: C 94.38, 94.02; H 5.94, 5.90. M 285.1, 288.0. $C_{24}H_{18}$. Calculated %: C 94.11; H 5.89. M 306.

Oxidation of 1,2-diphenyl-1-α-naphthylethylene. 3.06 g of the substance in 5 ml of ether was oxidized with 600 ml of a 2% solution of potassium permanganate in the presence of 5 g of sodium bicarbonate; phenyl-α-naphthyl ketone with a m. p. of 73-75° (from alcohol), which displayed no depression in a test of a mixture with the known preparation, and benzoic acid with a m. p. of 119-120° (from hot water), which displayed no depression with known benzoic acid, were isolated.

The resulting oxidation products demonstrated the structure of the hydrocarbon as 1,2-diphenyl-1-α-naphthylethylene.

1,2-Diphenyl-1-α-naphthyl-2-bromoethylene. 4 g of 1,2-diphenyl-1-α-naphthylethylene in 40 ml of glacial acetic acid was brominated with 2.2 g of bromine in 15 ml of glacial acetic acid. On pouring into water, a yellowish, sticky precipitate formed, which had no definite melting point after recrystallization from alcohol in the presence of activated carbon. The slightly yellowish, crystalline powder dissolved readily in benzene, ether and acetone, and slightly in alcohol (more readily in hot). An ether solution of the substance decolorized an aqueous solution of potassium permanganate.

Found %: Br 21.12, 21.13. M 336.8, 357.8. $C_{24}H_{17}Br$. Calculated %: Br 20.73. M 358.05.

Bromination of phenyl-α-naphthylbenzylcarbinol. 6.5 g of the carbinol in 50 ml of glacial acetic acid was brominated by 1.6 g of bromine in 15 ml of glacial acetic acid. Besides 0.78 g of a substance with a m. p. of 193-196° (from alcohol), 7.5 g of a substance (93.75% with respect to the carbinol) with a m. p. of 84-87° was formed, which displayed the same properties as the bromide synthesized by the action of bromine on 1,2-diphenyl-1-α-naphthylethylene.

Found %: Br 21.12, 20.93. $C_{24}H_{17}Br$. Calculated %: Br 20.73.

Oxidation of 1,2-diphenyl-1-α-naphthyl-2-bromoethylene. 3.86 g of a substance in 5 ml of ether was oxidized by 600 ml of a 2% solution of potassium permanganate, in the presence of 2 g of sodium carbonate; after extraction of the precipitate with hot alcohol, a substance with a m. p. of 73-74.5° was separated, which displayed no depression in a test of a mixture with phenyl α-naphthyl ketone.

From the aqueous filtrate, after acidification with sulfuric acid, a substance with a m. p. of 118-121° was isolated, which displayed no depression in a test of a mixture with benzoic acid. Bromide ion was detected by silver nitrate in the aqueous filtrate after acidification with nitric acid and after separation of the benzoic acid.

Thus, phenyl-α-naphthyl ketone, benzoic acid and bromide ion were found among the products of the oxidation of the substance with a m. p. of 84-87°, which demonstrated the structure of 1,2-diphenyl-1-α-naphthyl-2-bromoethylene.

Phenylbenzyl-β-naphthylcarbinol was obtained according to Berliner [8]; 7.2 g (36.8%) of a substance with a m. p. of 109.5-111° (from alcohol) was obtained from 2.4 g of magnesium, 12.7 g of benzyl chloride and 14 g of phenyl-β-naphthyl ketone in 100 ml of ether. A test of a mixture with known phenylbenzyl-β-naphthylcarbinol displayed no depression; moreover, benzyl alcohol and bibenzyl were formed.

1,2-Diphenyl-1-β-naphthylethylene. 5 g of phenyl-β-naphthylbenzylcarbinol in 40 ml of benzene was heated with 5 g of fused potassium bisulfate for 1 hour at 80°. After vacuum distillation of the benzene, the colorless, transparent solution was a viscous, slightly yellowish, clear substance, which was readily soluble in ether, acetone, chloroform and benzene, and slightly soluble in cold, but more readily in hot, alcohol. An attempt to crystallize it was unsuccessful.

Found %: C 94.03, 93.99; H 5.79, 5.70. M 316.61, 316.29. $C_{24}H_{18}$. Calculated %: C 94.11; H 5.8. M 306.

Oxidation of 1,2-diphenyl-1-β-naphthylethylene. 3 g of the substance in 5 ml of ether was oxidized in the cold with 500 ml of a 2% solution of potassium permanganate containing 5 g of sodium bicarbonate. After removal of the solution, the manganese peroxide was extracted with hot alcohol; from the latter, a substance with a m. p. of 82° was separated, which displayed no depression in a test of a mixture with known phenyl-β-naphthyl ketone. From the aqueous filtrate, after acidification with sulfuric acid, a substance with a m. p. of 121-122° was isolated, which showed no depression in a test of a mixture with known benzoic acid. On the basis of the resulting data, the structure of the hydrocarbon was demonstrated as 1,2-diphenyl-1-β-naphthylethylene.

1,2-Diphenyl-1-β-naphthyl-2-bromoethylene. 1.25 g of phenylbenzyl-β-naphthylcarbinol and 1 g of dioxane dibromide were heated on a water bath until removal of the hydrogen bromide. After extraction with ether and after removal of the latter, 0.8 g (54.4%) of a substance with a m. p. of 206-206.5° (from alcohol) and a resinous deposit which was not closely investigated, were isolated.

Found %: Br 19.87, 20.29. $C_{24}H_{17}Br$. Calculated %: Br 20.73.

Oxidation of 1,2-diphenyl-1-β-naphthyl-2-bromoethylene. 3 g of the substance with a m. p. of 206-206.5° was oxidized with a potassium permanganate solution in the presence of sodium carbonate under the conditions described above for the oxidation of the α-naphthyl isomer; then a substance with a m. p. of 82° which was identical to phenyl β-naphthyl ketone (test of a mixture displayed no depression) and benzoic acid with a m. p. of

120-121° (which displayed no depression with known benzoic acid) were isolated, and bromide-ion was detected (with $AgNO_3$). On the basis of the analytical data of the oxidation, the 1,2-diphenyl-1-β-naphthyl-2-bromoethylene structure corresponded to the substance with a m. p. of 206-206.5°.

We express appreciation to T. A. Melnikovaya for carrying out the biological investigations.

SUMMARY

1. The synthesis reaction of the isomeric phenyl-α- and β-naphthylbenzylcarbinols from benzylmagnesium chloride and the isomeric phenyl naphthyl ketones was investigated, and the structure of the latter was studied.

2. The dehydration reaction of phenyl-α- and β-naphthylbenzylcarbinols was investigated, and the corresponding isomeric unsaturated hydrocarbons formed, the structure of which was demonstrated by oxidation.

3. The bromination reaction of the isomeric diphenylnaphthylethylenes was investigated; whereupon it was found that bromine replaces the hydrogen of the ethylene group. Moreover, it was shown that the synthesis of isomeric diphenylnaphthylbromoethylenes may be carried out by the direct bromination of isomeric phenylbenzylnaphthylcarbinols.

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INVESTIGATION IN THE FIELD OF CATALYTIC CONVERSION OF ALCOHOLS TO HYDROCARBONS OF THE BIVINYL SERIES

XIX. HEXADIENE-1,3 IN THE TRANSFORMATION PRODUCTS OF MIXTURES OF ETHYL AND BUTYL ALCOHOLS

Yu. A. Gorin, N. G. Belenkaya, V. S. Ivanov and A. P. Kavunenko

S. V. Lebedev, studying the composition of the by-products which formed with bivinyl from ethyl alcohol, found among them hydrocarbons containing 6 carbon atoms, particularly, hexadiene-2,4 [1]. I. A. Livshits and S. I. Ilyina [2] showed that hexadiene-2,4 was one of the products of the contact transformation of a mixture of butyl alcohol and acetic anhydride over S. V. Lebedev's catalyst. In this case, the formation of hexadiene-2,4 was explained by the authors on the basis of Yu. A. Gorin's ideas of the reaction mechanism [3] of the catalytic formation of bivinyl from the alcohol (via crotonaldehyde).

Scheme of Formation of Hexadiene-2,4

1. $CH_3-CH_2-CH_2-CH_2OH \longrightarrow CH_3-CH_2-CH_2-CHO + H_2$.
2. $CH_3-CH_2-CH_2-CHO + CH_3-CHO \longrightarrow [CH_3-CH_2-CH_2-CHOH-CH_2-CHO] \longrightarrow$
   $\longrightarrow H_2O + CH_3-CH_2-CH=CH-CHO$.
3. $CH_3-CH_2-CH_2-CH=CH-CHO + 2H \longrightarrow CH_3-CH_2-CH_2-CH=CH-CH_2OH$.
4. $CH_3-CH_2-CH_2-CH=CH-CH_2OH \longrightarrow H_2O + CH_3-CH=CH-CH=CH-CH_3$.

Acetaldehyde, butyl alcohol and butyraldehyde were also by-products in the production of bivinyl from ethyl alcohol. According to the specified scheme their reaction explained the formation of hexadiene-2,4 in S. V. Lebedev's reaction.

Let us consider Reaction 4 of the Scheme. It can be assumed that hexadiene-1,3 will be the chief dehydration product of the unsaturated alcohol (hexen-2-ol-1). The former, under the reaction conditions, under the influence of a high temperature (about 400°) and of a catalyst, especially of its dehydrating component, which also has isomerizing properties [1], may be completely or partially converted to the more stable isomer, hexadiene-2,4. It should be observed that instances of such a type of isomerization, proceeding under the influence of different factors and connected with the transfer of the system of conjugated double bonds at the end of the hydrocarbon molecule to the middle, are repeatedly described in the literature [4].

The present work, set up for the investigation of the feasibility of the catalytic formation of hexadiene-1,3 from a mixture of ethyl and butyl alcohols under S. V. Lebedev's reaction conditions, confirmed our assumptions.

Among the products of the catalytic conversion of a mixture of ethyl and butyl alcohols, together with hexadiene-2,4, we found a certain quantity of hexadiene-1,3, which was the chief component of the C_6 hydrocarbons. The total yield of the C_6 hydrocarbons (b. p. from 60-80.5°) under the conditions which we adopted amounted to about 5% by weight of the mixture passed. The ratio of hexadiene-1,3 to hexadiene-2,4 was approximately 1:3.

The structure of the hexadienes (-1,3 and -2,4) which we obtained was demonstrated by the determination of their physico-chemical constants (which agreed with the literature values), by establishment of the elementary composition and molecular weight, by obtaining the tetrabromides, and by hydrogenation. The presence in the resulting hydrocarbons of a system of conjugated double bonds was demonstrated by the formation of insoluble sulfone polymers by the action of sulfurous anhydride, the formation of crystalline derivatives with maleic anhydride and with α-naphthoquinone, and by exaltation of the molecular refraction. The position of the system of conjugated bonds was

established by the oxidation of the dehydrogenated α-naphthoquinone addition product. For hexadiene-1,3, anthraquinone monocarboxylic acid was obtained, and for hexadiene-2,4 anthraquinone dicarboxylic acid was obtained.

The production of hexadiene-1,3, together with hexadiene-2,4, from a mixture of ethyl and butyl alcohols in our experiments deepened the concepts of the mechanism of the catalytic formation of diene hydrocarbons from alcohols, and explained the presence of the C_6H_{10} hydrocarbons among the by-products of the contact synthesis of bivinyl by S. V. Lebedev's method.

EXPERIMENTAL

Materials, apparatus and experimental conditions. The following were used as starting materials: 1) 95% ethyl alcohol – distillate d_4^{20} 0.8132; 2) butyl fermentation alcohol from which a fraction with a b. p. of 116-117°, d_4^{20} 0.8112, n_D^{20} 1.3988 was separated by distillation.

The contacting of the mixture of ethyl and butyl alcohols was carried out in a laboratory furnace of 70 cm length, mounted obliquely. 150 ml of S. V. Lebedev's catalyst [1] was charged into a 2.8 cm-diameter quartz tube in the constant temperature zone. After each experiment, the catalyst was regenerated at 500° in a current of air for 2 hours.

Experiments were carried out with mixtures of ethyl and butyl alcohols, taken in molar ratios of 1:1 and 1:2, in order to determine the conditions of formation of the liquid hydrocarbons. In each experiment about 100 ml of the mixture was passed through the furnace at 380° at the rate of 1 ml/min. The reaction products, after discharge from the furnace, passed through a condenser, and the condensate was collected in a vessel cooled with ice. The condensate consisted of two layers. The upper oil layer was separated from the lower aqueous layer, and was washed with a constant volume of water. The final washing was made with a hydroxylamine hydrochloride solution in order to remove the carbonyl compounds. The results of these experiments showed that larger hydrocarbon yields were obtained with a 1:2 ratio of starting materials than with a 1:1 ratio.

For the purpose of accumulating sufficient quantities of the hydrocarbons, 20 experiments were carried out with a 1:2 ratio under the conditions specified above. 1632.5 g of the mixture of alcohols was passed in portions of about 100 ml over the catalyst. The yield of the hydrocarbons, washed with water and dried over calcium chloride, was 419.5 g (25% by weight). In order to remove impurities, the dried hydrocarbons were treated with metallic sodium in the cold. The hydrocarbons were removed from the resinified portion at low vacuum (200 mm) in a nitrogen atmosphere on a heating bath at about 95° (360 g of hydrocarbons was obtained).

The removed hydrocarbons were distilled in a nitrogen atmosphere with a branched fractionating column. 256.3 g was used in the distillation, and the fractions obtained were: Fr. 1, b. p. 60°, 3.8%; Fr. 2, b. p. 60-90°, 54.6%; Fr. 3, b. p. 90-115°, 2.0%; Fr. 4, b. p. 115-126°, 17.0%; Fr. 5, b. p. 126-132°, 11.7%; Residue and losses 10.6%.

The 60-90° fraction, in which the main bulk of the C_6 hydrocarbons was probably included, was repeatedly treated in a 75.5 g quantity by heating at about 100°, with metallic sodium until the sodium was dissolved. 55.95 g of pure hydrocarbons was obtained after removal from the resin. This mixture was distilled by a column with metal caps, with a separating capacity of 45 theoretical plates. 55.9 g was used in the distillation, and the fractions obtained were: Fr. 1, b. p. 62.0-70.0°, 27.0%; Fr. 2, b. p. 70.0-72.0°, 3.1%; Fr. 3, b. p. 72.0-73.0°, 7.3%; Fr. 4, b. p. 73.0-79.0°, 16.8%; Fr. 5, b. p. 79.0-80.5°, 21.2%; Residue and losses 24.6%. The 72-73° fraction, which corresponded to hexadiene-1,3, and the 79.0-80.5° fraction, which corresponded to hexadiene-2,4, were studied in greater detail. The remaining fractions were not examined.

Investigation of the Fraction with a b. p. of 72-73°

d_4^{20} 0.7114, n_D^{20} 1.4392, MR_D 30.39; calc. 28.97, EMR_D 1.42. Literature values for hexadiene-1,3: b. p. 72.9°, d_4^{20} 0.7070, n_D^{20} 1.4402 [5].

Found %: C 87.74; H 12.46. M 81.2. C_6H_{10}. Calculated %: C 87.73; H 12.27. M 82.14.

Action of a saturated solution of SO_2. A white tablet of the sulfone polymer of the hydrocarbon with a system of conjugated double bonds was formed by shaking a sample of the fraction with a saturated aqueous solution of SO_2.

Hydrogenation. A weighed portion of the fraction in an alcohol solution was hydrogenated to complete saturation over platinum black in S. V. Lebedev's apparatus [6]. The hydrogenation product was salted out of the alcohol with a saturated solution of sodium chloride, dried with calcium chloride and distilled over metallic sodium. The resulting saturated hydrocarbon was identified as n-hexane.

B. p. 68-69°, d_4^{20} 0.6605, n_D^{20} 1.3756. According to the literature, for n-hexane, b. p. 68.4-68.8°, d_4^{20} 0.6603, n_D^{20} 1.37536 [7].

The bromination of the hydrocarbon was carried out in a chloroform solution with cooling to −20° [8]. The chloroform was driven off in vacuo; in the flask an oily liquid remained, the major portion of which crystallized. The crystals, recrystallized twice from petroleum ether, melted at 91.5-92°. According to the literature, the melting point of 1,2,3,4-tetrabromohexane is 91-92° [8, 9].

Found %: Br 79.25 (Carius). $C_6H_{10}Br_4$. Calculated %: Br 79.58.

Reaction with maleic anhydride. An evolution of heat was observed on pouring together the fraction to be investigated and a benzene solution of maleic anhydride. After further heating of the mixture and after removal of the benzene, the residue was washed free of the unreacted maleic anhydride with several portions of hot water, and was dried in a vacuum-desiccator. Crystals with a m. p. of 51-52° were obtained after 2 recrystallizations from petroleum ether. According to the literature, the product of the reaction of hexadiene-1,3 and maleic anhydride melts at 52° [5].

Condensation with α-naphthoquinone and production of anthraquinone monocarboxylic acid. The condensation with α-naphthoquinone was carried out according to [10]. The α-naphthoquinone, first recrystallized from petroleum ether, had a m. p. of 125°.

2.8 g of α-naphthoquinone was added to 1.5 g of the fraction in 7 ml of alcohol. The mixture was heated for 3 hours on a boiling water bath. On cooling, a solution of 0.1 g of KOH in 25 ml of ethyl alcohol was added to the darkened solution, after which air was drawn through the liquid for half an hour. The solution warmed up spontaneously at first, then it was heated gently on the water bath. Yellow crystals were formed from the wine-red solution. Recrystallized twice from ethyl alcohol, the dehydrogenation product melted at 82-83°.

The resulting dehydrogenation product was oxidized further according to Elbs [11]. 0.4 g of this product was heated in a glass tube in a thermostat for 2 hours, at 170° with 7 ml of nitric acid (d 1.1), after which a discharge of gases resulted, and then it was heated for 3 hours at 200-220°. On cooling, bright-yellow acicular crystals precipitated. After recrystallization from glacial acetic acid, the product melted at about 280°; moreover, it darkened. Because of the small quantity of the crystals, no second recrystallization was carried out.

Found: equiv. 251 (by titration in an alcoholic solution). $C_{14}H_7O_2(COOH)$. Calculated: equiv. 252.

Investigation of the Fraction with a b. p. of 79.0-80.5°

d_4^{20} 0.7233, n_D^{20} 1.4490, MR_D 30.41; calc. 29.97, EMR_D 1.44. Literature values for hexadiene-2,4: b. p. 80°, d_4^{20} 0.720, n_D^{20} 1.4514 [12].

A bromination was carried out in a chloroform solution, with stirring. After removal of the chloroform and after recrystallization from ethyl alcohol, crystals which melted at 179.5° were obtained. According to the literature, the m. p. for 2,3,4,5-tetrabromohexane is 181.2-182° [13].

The reaction with maleic anhydride was carried out as described above. An evolution of heat and a change of color were observed on pouring together the hydrocarbon and a benzene solution of maleic anhydride. The crystalline substance which remained after removal of the benzene was washed with hot water in order to remove the excess maleic anhydride, and was recrystallized 3 times from ligroine. The resulting crystals melted at 94-95°. According to the literature, the reaction product of maleic anhydride and hexadiene-2,4 melts at 95-96° [14].

Condensation with α-naphthoquinone and production of anthraquinone dicarboxylic acid. All the operations were carried out as described above. 2.2 g of the fraction, 10 ml of alcohol and 4 g of α-naphthoquinone were used. After recrystallization from glacial acetic acid, the resulting anthraquinone dicarboxylic acid (bright-yellow crystals) had a m. p. of 287°. In this case, also, the product was not recrystallized again.

Found: equiv. 151. $C_{14}H_6O_2(COOH)_2$. Calculated: equiv. 148.

SUMMARY

1. The transformation of a mixture of ethyl and butyl alcohols, taken in a 1:2 ratio, over S. V. Lebedev's catalyst at 380°, was investigated.

2. It was shown that a certain quantity of hexadiene-1,3, together with hexadiene-2,4, formed at this time. Under the conditions indicated above, the ratio between the hexadienes-1,3 and -2,4 was 1:3.

3. There has been set forth a possible scheme of formation of hexadiene-1,3 from a mixture of ethyl and butyl alcohols, and of the formation of hexadiene-2,4 by the isomerization of hexadiene-1,3.

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" INTERMOLECULAR AND INTRAMOLECULAR OXIDATION-REDUCTION"

IV. HYDROGENATION OF HYDROXYL GROUP AND MULTIPLE BONDS IN UNSATURATED ALCOHOLS

N. S. Tikhomirova-Sidorova

The hydrogenation of aliphatic-aromatic alcohols with the retention of the alcoholic group and production of the cyclohexyl radical was especially difficult in a synthetic respect and was of interest.

In the solution of the problem of the synthesis of such alcohols we were confronted with the extremely easy displacement of the alcoholic hydroxyl hydrogen by an aromatic ring of great inertia, as a result of which, besides the alcohols with a cyclohexyl radical, aromatic hydrocarbons were obtained. Our experiments also provided some material for the solution of problems of the resistance of hydroxyl groups to reduction under the influence of atoms or radicals entering into the molecule, on which the entire course of the hydrogenation also strongly depends.

In our experiments, benzyl alcohol, for which a phenyl nucleus was on the alcoholic group carbon, and cinnamic alcohol, for which a phenyl nucleus was remote from the alcoholic group, were hydrogenated.

The hydrogenation was carried out under identical conditions, whereupon the benzyl alcohol, hydrogenating chiefly to toluene, yielded 20% cyclohexylcarbinol, without recovery of the initial alcohol.

$$C_6H_5-CH_2OH \longrightarrow C_6H_5-CH_3 + C_6H_{11}-CH_2OH.$$

As a result of the hydrogenation of cinnamic alcohol, in not one experiment was the hydrogenation of the aromatic ring observed; phenyl propyl alcohol formed, which further gave 50% propylbenzene and was recovered by 50%; the ring was not hydrogenated at all, but the alcoholic group hydrogenated more sluggishly than it did for benzyl alcohol.

$$C_6H_5-CH=CH-CH_2OH \longrightarrow C_6H_5-CH_2-CH_2-CH_3 + C_6H_5-CH_2-CH_2-CH_2OH.$$

Consequently, the hydroxyl group, in the vicinity of which was the phenyl radical, had the least stability. We reported earlier [1] that in the oxidation-reduction conversions of the α-keto alcohols the keto alcoholic grouping in the presence of the phenyl radical in the α-position to it (for example, benzoin), was also found to be least stable.

If we consider the relative ease of hydrogenation of benzene and phenol to the cyclohexane derivatives, then it becomes clear that the difficulty in obtaining alcohols with a cyclohexyl radical is connected with the presence of the alcoholic group; it is reduced more readily to alkyl radical than the aromatic ring hydrogenates, and more difficultly than the hydrogenation of the double bond proceeds.

On hydrogenation of the acetates of benzyl and cinnamic alcohols under the conditions of hydrogenation of the same alcohols, the corresponding hydrocarbon and acetic acid were obtained.

Furthermore, the experiments on the catalytic hydrogenation of alcohols with accumulation of sufficient material, must aid the solution of the total problem of the oxidation-reduction transformations of hydroxycarbonyl compounds (hydroxy aldehydes and hydroxy ketones).

EXPERIMENTAL

The hydrogenation was carried out in a 500 ml rotating autoclave, which was installed in a furnace with an electric heater. Ethyl alcohol was used as the solvent. The catalyst was Raney nickel prepared as indicated in the

literature [2]. Benzyl alcohol (b. p. 204-205°) and cinnamic alcohol (b. p. 150-151° at 27 mm, m. p. 32.5°) were used for the experiments.

The acetates of benzyl and cinnamic alcohols were prepared by acetylation of the corresponding alcohols and had the following properties:

Benzylacetate b. p. 111° at 25 mm, n_D^{20} 1.5222; acetate of cinnamic alcohol b. p. 134° at 10 mm, n_D^{20} 1.5428, d_4^{20} 1.0515.

We judged the products which were obtained by hydrogenation from the quantity of hydrogen consumed and from the analysis of the substances obtained.

Hydrogenation of benzyl alcohol. In the series of experiments, the hydrogenation led to a mixture of cyclohexylcarbinol and toluene, without the recovery of benzyl alcohol.

For example, 60 g (0.56 mole) of benzyl alcohol, 60 ml of ethyl alcohol and 2 g of catalyst were used. Hydrogenation was begun at 200° and 165 atm, and was continued for 1 hour 15 minutes, during which the temperature was maintained at 190-200°. The initial pressure was 108 atm, and the final pressure was 38 atm. The pressure drop of 70 atm corresponded to 26.5 liters or 2.3 g of hydrogen. 1.1 g of hydrogen was required for the hydrogenation of 60 g of benzyl alcohol to toluene, and 3.6 g was required for its hydrogenation to cyclohexylcarbinol.

11.7 g (18.6%) of cyclohexylcarbinol with a b. p. of 90° (18 mm) and 29 g (63%) of toluene with a b. p. of 25° (50 mm) were isolated from the reaction mixture.

Benzyl acetate, toluene and acetic acid were obtained in a quantitative yield on hydrogenation under the same conditions (160 atm, 190°).

Properties of cyclohexylcarbinol: b. p. 90° (18 mm), 83° (10 mm), n_D^{20} 1.4630, d_4^{20} 0.9207, MR_D 34.19. $C_7H_{14}O$. calc. 33.85.

Found: active H 0.945, 0.965. $C_7H_{14}O$. Calculated: active H 1.00.

Hydrogenation of cinnamic alcohol. 1, 2, 4, or 5 moles of hydrogen, respectively, was required for 1 mole of cinnamic alcohol for the production of hydrocinnamic alcohol, propylbenzene, 3-cyclohexylpropanol-1 or propylcyclohexane. In our experiments 1.8 moles of hydrogen, on an average, was consumed for 1 mole of cinnamic alcohol. The hydrogenation proceeded chiefly to propylbenzene. However, under optimum conditions about a 50% yield of hydrocinnamic alcohol was obtained.

For example, 75 g of cinnamic alcohol, 85 g of ethyl alcohol and 5 g of catalyst were used. The initial pressure was 100 atm. Hydrogenation was begun at 195° and 160 atm and was continued for 45 minutes, during which the temperature was kept at 190-200°. The final pressure was 30 atm, which corresponded to 23.2 liters or 2.09 g of hydrogen.

The following fractions were separated after the usual treatment and after vacuum distillation:

Fr. 1, 19-20° (30 mm), 30 g, n_D^{18} 1.3868. Fr. 2, 38-43° (14 mm), 7 g, n_D^{20} 1.4919, d_4^{20} 0.8555. Fr. 3, 120° (14 mm), 40 g, n_D^{20} 1.5195, d_4^{20} 0.9848.

According to the literature for propylbenzene [3]: n_D^{20} 1.4925, d_4^{20} 0.8622; for hydrocinnamic alcohol [4]: n_D^{17} 1.5280, d_4^{24} 0.995.

The first fraction was a mixture of ethyl alcohol and propylbenzene, the 2nd fraction was propylbenzene, and the 3rd fraction was hydrocinnamic alcohol.

For hydrocinnamic alcohol MR_D 41.89. $C_9H_{12}O$. calc. 41.67.

The phenylurethan of hydrocinnamic alcohol with a m. p. of 48° (from alcohol) was obtained by the usual method.

According to the literature, a m. p. of 45° corresponded to the phenylurethan of hydrocinnamic alcohol, and a m. p. of 88° [6] corresponded to that for 3-cyclohexylpropanol-1.

Found %: N 5.92, 5.89. $C_{16}H_{17}O_2N$. Calculated %: N 5.60.

For further demonstration that the hydrocinnamic alcohol, but not 3-cyclohexylpropanol-1, was obtained, the resulting product was oxidized with sodium bichromate. A product was obtained which gave a silver mirror reaction,

and had a b. p. of 105-106° (14 mm), as indicated in the literature for hydrocinnamic aldehyde [7]. The semicarbazone (m. p. 127°) and the p-nitrophenylhydrazone (m. p. 122-123°), which corresponded to the literature value for hydrocinnamic aldehyde [7, 8] were obtained from the aldehyde by the usual method.

Thus, the aromatic ring of cinnamic alcohol was not hydrogenated. On hydrogenation of the acetate of cinnamic alcohol, acetic acid and propylbenzene were formed.

We express sincere appreciation to Prof. S. N. Danilov for his guidance of the work.

SUMMARY

1. The hydrogenation of benzyl and cinnamic alcohols was carried out for the purpose of conversion to the corresponding alcohols with a cyclohexyl radical.

2. On the basis of the literature values and of our experiments, it can be stated that under these conditions, the benzyl alcohol in which the phenyl is hydrogenated quantitatively to cyclohexanol, is hydrogenated chiefly to toluene, giving 20% cyclohexylcarbinol, without recovery of the initial alcohol. 50% of the phenyl propyl alcohol (which formed as a result of the hydrogenation of cinnamic alcohol) formed propylbenzene and 50% was recovered, i. e., in this case the aromatic ring did not hydrogenate at all, and the alcoholic group hydrogenated more sluggishly than it did for benzyl alcohol.

3. The hydroxyl group, in the α-position to which was the phenyl radical, had the least stability of the alcohols considered.

For the oxidation-reduction conversions of α-keto alcohols, the keto-alcoholic grouping in the presence of phenyl radical in the α-position proved to be the least stable.

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ELECTROLYTIC HYDROGENATION OF ALIPHATIC-AROMATIC ACETYLENE ALCOHOLS

A. I. Lebedeva and T. A. Mishnina

It was shown by A. E. Favorsky and his students [1] that multistage electrolytic hydrogenation of aliphatic series tertiary acetylene alcohols proceeds at copper or silver-plated cathodes in an alkaline electrolyte, with the formation of the corresponding ethylenic alcohols. However, it had not been established until recently how the process occurred for acetylenic alcohols with aliphatic-aromatic and aromatic substituents. In the present work we decided to study this problem, and undertook the electrolytic hydrogenation of methyl-p-tolyl- and phenyl-p-tolylacetylenecarbinol.

The hydrogenation was carried out in a water-alcohol alkaline medium at copper oxide-coated copper or silver-plated cathodes with separation of the electrodes by a porous diaphragm. It was shown that under these conditions, as for the aliphatic acetylene alcohols, a selective hydrogenation proceeded, with the formation of methyl-p-tolyl- and phenyl-p-tolylvinylcarbinols. The best results were obtained by hydrogenation at silver-plated copper cathodes. In all probability, copper or silver-acetylene complexes participate in the hydrogenation process. Whether this complex is reduced directly or whether it undergoes dissociation before reduction cannot be established without additional investigations. It was inferred from Delahay and Berzins' works [2] that both of these processes were entirely probable in the reduction of the complexes.

We obtained the acetylene alcohols in a yield of about 80% from the appropriate ketones and acetylene by Favorsky's method, developed for such alcohols by I. A. Favorskaya and L. F. Fedorova [3].

The condensation reaction of acetylene and methyl-p-tolyl- and phenyl-p-tolyl ketones proceeds so well that almost no acetylene glycols form. Phenyl-p-tolylacetylenecarbinol was extremely stable in an alcoholic medium. On distillation in the presence of traces of alkali it decomposed into its initial components. The structure of the resulting ethylene alcohols was demonstrated by catalytic hydrogenation in the presence of platinum black.

Only polymeric products of unestablished structure were obtained by the dehydration of methyl-p-tolylvinylcarbinol under different conditions (dilution with isoamyl alcohol, etc.).

EXPERIMENTAL

Methyl-p-tolylacetylenecarbinol with a m. p. of 34-35° was obtained according to the preceding [4]. Phenyl-p-tolylacetylenecarbinol (18.8 g) was obtained from 15 g of phenyl-p-tolyl ketone and 100 g of powdered KOH in 400 ml of ether. 103% H_2 (of calculated for 2 H_2 molecules) was added during the catalytic hydrogenation of 3.0 g of phenyl-p-tolylacetylenecarbinol (0.3 g of Pt, 80 ml alcohol). Phenyl-p-tolylethylcarbinol was obtained after removal of the solvent.

The electrolytic hydrogenation of methyl-p-tolyl- and phenyl-p-tolylacetylenecarbinols was carried out by a method described for diethylacetylenecarbinol [5]. The catholyte consisted of 10 g of the carbinol, 150 ml of C_2H_5OH, 50 ml of water, and 0.5 g of NaOH. 3.4 ampere-hours was calculated, but 9.2 ampere-hours was required. 8 g of methyl-p-tolylvinylcarbinol was obtained, in the catalytic hydrogenation of which (2.0 g of the carbinol, 0.2 g of Pt, 80 ml of alcohol) 97.5% H_2 was absorbed. Methyl-p-tolylethylcarbinol was obtained after removal of the solvent.

The electrolytic hydrogenation of phenyl-p-tolylacetylenecarbinol was carried out according to the preceding. From 10 g, 8 g of phenyl-p-tolylvinylcarbinol was obtained, in the catalytic hydrogenation of which (3 g of carbinol, 0.3 g Pt, 80 ml of alcohol) 100.1% of H_2 was absorbed. Phenyl-p-tolylethylcarbinol was obtained after removal of the solvent. The results of the analyses for all of the compounds which were obtained for the first time are cited in the Table.

Name of compound	Boiling point at a pressure (mm) of	d_4^{20}	n_D^{20}	Found %		Number of active H-atoms*	Calculated %	
				C	H		C	H
Methyl-p-tolylvinyl-carbinol	97-97.5° (5)	0.9893	1.5295	81.82	8.47	1.06	81.44	8.70
Methyl-p-tolylethyl-carbinol	93-93.5 (3)	0.9726	1.5174	80.23	9.84	1.07	80.45	9.82
Phenyl-p-tolylacetylene-carbinol **	153-154 (4)	1.0837	1.5868	86.38	6.62	1.03	86.45	6.35
Phenyl-p-tolylvinyl-carbinol	157-158 (3)	1.0650	1.5792	–	–	1.00	–	–
Phenyl-p-tolylethyl-carbinol	154-155 (3)	1.0512	1.5779	–	–	0.96	–	–

* Number of active H-atoms calculated: 1.00.

** Found M 220.3; calculated 222.27.

SUMMARY

1. It was found that the aliphatic-aromatic acetylene alcohols, methyl-p-tolyl- and phenyl-p-tolylacetylene-carbinols, were selectively hydrogenated to the corresponding ethylenic alcohols in an alkaline water-alcohol electrolyte at silver-plated copper cathodes.

2. The following alcohols were obtained for the first time: methyl-p-tolylvinyl-, methyl-p-tolylethyl-, phenyl-p-tolylacetylene-, phenyl-p-tolylvinyl- and phenyl-p-tolylethylcarbinols.

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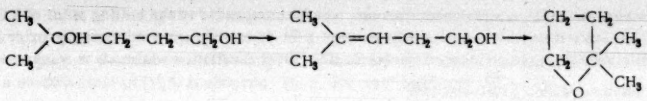
THE MECHANISM OF DEHYDRATION OF γ-GLYCOLS

I. STUDY OF THE DEHYDRATION OF 2-METHYLPENTANEDIOL-2,5 AND 2-PHENYLPENTANEDIOL-2,5

T. A. Favorskaya and O. V. Sergievskaya

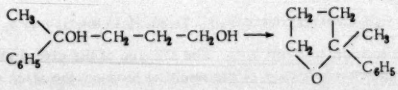
One of us and N. V. Shcherbinskaya [1, 2] found that, on distillation with traces of acid, the primary β-ethylene alcohols, 2-methylpenten-2-ol-5 and 3-methylhexen-3-ol-6, isomerized to the tetrahydrofuran derivatives. Such a mechanism of the formation of the tetrahydrofuran derivatives forced us to assume that the formation of tetrahydrofuran derivatives by the dehydration of γ-glycols can result, not in the formation of water due to the two glycol hydroxyls, as was first proposed by Wallach [3] and until now was used by all investigators, but can result in the intermediate formation of an unsaturated β-ethylene alcohol, which, under the conditions of dehydration in an acid medium, isomerizes to the tetrahydrofuran derivative.

In order to verify this assumption, the dehydration of two primary-tertiary γ-glycols, 2-methylpentanediol-2,5 (I) and 2-phenylpentanediol-2,5 (IV), was studied in the present work. For the first glycol a dilute sulfuric acid concentration was selected, which brought about the dehydration of the glycol with the formation of the unsaturated alcohol, and the pH of this acid was determined and found to be equal to 1.6. Then the resulting unsaturated alcohol (II) was isomerized to 2,2-dimethyltetrahydrofuran (III):



(I) (II) (III)

It was found each time in a study of the dehydration of the second glycol that, on heating it under different conditions with sulfuric acid of pH 1.6, no unsaturated alcohol, 2-phenylpenten-2-ol-5 (VI), was obtained, but its corresponding tetrahydrofuran derivative 2,2-methylphenyltetrahydrofuran (V), was obtained:



(IV) (V)

The same result was also obtained by heating the glycol with orthophosphoric acid (pH 1.57), with formic acid (pH 2.4) and with a buffer mixture consisting of acetic acid and sodium acetate (pH 3.7).

Because it was shown earlier [4] that the unsaturated alcohol, 2-phenylpenten-2-ol-5, which formed on reaction of methylphenylcyclopropylcarbinol with formic acid (1:1)

$$CH_3(C_6H_5)C{=}CH{-}CH_2{-}CH_2OH\ (VI),$$

unlike the other alcohols studied under these conditions, was not converted to the tetrahydrofuran derivative (V), it was decided to obtain this alcohol and to attempt to convert it to the oxide (V) under different conditions.

2-Phenylpenten-2-ol-5 (VI) was obtained from methylphenylcyclopropylcarbinol by a method developed by Shcherbinskaya [4]. On the reaction of this alcohol with 85% formic acid the yield of (V) amounted to 50%; on reaction with 60% formic acid the yield of (V) amounted to 48%; on heating the same alcohol with sulfuric acid (1:3) an 80% yield of (V) was obtained. The distillation of the alcohol (VI) at atmospheric pressure proceeded without any change; it was also not converted to (V) on distillation with drops of formic acid. The resulting data showed that

2-phenylpenten-2-ol-5 did not isomerize to the tetrahydrofuran derivative, which can be explained by the presence of a system of conjugated double bonds in its molecule. It was converted to the tetrahydrofuran (V) only under conditions in which the hydration of the double bond was possible, by heating with sufficiently concentrated acid; the glycol which formed at this time was converted directly to the γ-oxide, forming water due to its hydroxyl groups.

Attempts were made to convert the unsaturated alcohol (VI) to the glycol (IV), by the action of sulfuric acid in the cold, as Rupe [5] did in the production of 2-methylheptanediol-2,6 from 2-methylhepten-2-ol-6. However, on stirring (VI) with 25% sulfuric acid in the cold for 40 hours, all the alcohol was converted to (V), but on stirring for 30 hours with sulfuric acid (pH 1.6) it was recovered completely.

All the products obtained were investigated in detail in our laboratory earlier; therefore, their structure was not demonstrated in the present work.

EXPERIMENTAL

The synthesis of 2-methylpentanediol-2,5 (I) was carried out by the reaction of acetopropyl alcohol with methylmagnesium bromide. After the usual treatment, the glycol was extracted with ether manually and by an extractor. The glycol yield was about 20%.

B. p. 124-125° (17 mm), n_D^{20} 1.4501, d_4^{20} 0.9743, MR_D 32.55; calc. 32.95.

Literature values: b. p. 118-120° (14 mm) [6]; 108-110° (5 mm), n_D^{20} 1.4560, d_4^{20} 0.9817.

After the ether extractions of the glycol, the slightly acid solution which remained and still contained glycol was steam-distilled. In the distillate the unsaturated alcohol, 2-methylpenten-2-ol-5, was detected by its characteristic odor, suggestive of the odor of geranium. In the following experiment, after the decomposition of the organomagnesium complex with water and with sulfuric acid, the resulting solution was made slightly acid, the pH of this solution was determined and found to equal 1.6, and the solution was distilled. The product, extracted with ether and dried with K_2CO_3, boiled at 90-91° at atmospheric pressure, which corresponded to the boiling point of 2,2-dimethyltetrahydrofuran [1]. Since it is known that 2-methylpenten-2-ol-5, can be converted to the γ-oxide by distillation at atmospheric pressure in the presence of traces of acid, further distillation was made in vacuo.

The yield of the unsaturated alcohol (II) was 10%.

B. p. 59-60° (11 mm), d_4^{20} 0.8571, n_D^{20} 1.4440, MR_D 30.97; calc. 30.97 [1].

Found %: OH 17.34. $C_6H_{12}O$. Calculated %: OH 17.00.

The yield of the γ-oxide (III) was 20%.

B. p. 90-91°, d_4^{20} 0.8399, n_D^{20} 1.4058, MR_D 29.91; calc. 29.23 [1].

Found %: C 71.50; H 11.87. $C_6H_{12}O$. Calculated %: C 71.33; H 11.99.

Reaction of the glycol (I) with sulfuric acid (pH 1.6). The solution of the glycol obtained earlier in the sulfuric acid specified, was distilled; in the investigation of the resulting products the same alcohol and γ-oxide were separated. The resulting alcohol (II) was converted completely to (III) by distillation at atmospheric pressure with traces of sulfuric acid.

The synthesis of 2-phenylpentanediol-2,5 (IV) was carried out by the reaction of acetopropyl alcohol with phenylmagnesium bromide. After the usual treatment, the glycol was extracted with ether and was vacuum distilled. Its yield was 40-50%.

B. p. 162-163° (3 mm), d_4^{20} 1.0791, n_D^{20} 1.5340 [4].

Found %: OH 18.08. $C_{11}H_{16}O_2$. Calculated %: OH 18.88.

The reaction of 2-phenylpentanediol-2,5 (IV) with sulfuric acid (pH 1.6) was carried out under different conditions; the glycol and the acid were boiled under reflux for 6 hours. As a result, a 38% yield of 2,2-methylphenyltetrahydrofuran (V) was obtained. Heating of the glycol and the acid was carried out on the water bath at 60-70°. The yield of (V) was 22%. The glycol and the acid were poured together and distilled. The yield of (V) was 80%.

B. p. 107° (17 mm), d_4^{20} 1.0044, n_D^{20} 1.5178, MR_D 48.85; calc. 48.64 [7].

Found %: C 81.08; H 8.63. $C_{11}H_{14}O$. Calculated %: C 81.48; H 8.77.

In not one of these experiments were fractions corresponding to the alcohol (VI) obtained.

On distillation of the glycol with 0.1 N H_3PO_4 (pH 1.57) the yield of the tetrahydrofuran (V) amounted to 58%, on distillation with formic acid (pH 2.4) it was 50%, and with a buffer mixture of acetic acid and sodium acetate (pH 3.7) it was 9%. Besides the tetrahydrofuran (V), more or less of the initial glycol (IV) was obtained in all cases.

The synthesis of methylphenylcyclopropylcarbinol was carried out under conditions which Fridman developed [8], by the action of phenylmagnesium bromide on acetyltrimethylene. The yield was 60-75%.

B. p. 105-107° (3 mm), d_4^{20} 1.0386, n_D^{20} 1.5370, MR_D 49.00; calc. 49.42.

Found %: C 81.68; H 8.43; OH 9.89. $C_{11}H_{14}O$. Calculated %: C 81.48; H 8.64; OH 10.50.

58 g of the resulting alcohol was boiled with 60 ml of formic acid (1:1), with stirring for 1.5 hours. After neutralization with soda, extraction with ether and drying with potash, the reaction products were vacuum distilled: Fr. 1, 95-100° (9 mm), 11 g (19%), n_D^{20} 1.5426; Fr. 2, 133-135° (7 mm), 36 g (62%), n_D^{20} 1.5438.

The 1st fraction was Kizhner's hydrocarbon [9], phenylcyclopropylethylene, and gave a reaction with sulfuric acid and alcohol characteristic of it. The 2nd fraction, a mixture of 2-phenylpenten-2-ol-5 and its formate [4], was hydrolyzed by boiling with a 20% solution of potash for 23-25 hours. The yield of 2-phenylpenten-2-ol-5 (VI) was 50%.

B. p. 134-137° (2 mm), d_4^{20} 1.0179, n_D^{20} 1.5590, MR_D 51.30; calc. 50.45 [4].

Found %: C 81.22; H 8.66; OH 8.32. $C_{11}H_{14}O$. Calculated %: C 81.48; H 8.77; OH 10.50.

On distillation under atmospheric pressure the unsaturated alcohol (VI) boiled at 268-269°, n_D^{20} 1.5569. No isomerization to the tetrahydrofuran (V) was observed either in this case or on distillation with drops of concentrated formic acid.

As a result of heating the unsaturated alcohol (VI) for 1 hour with concentrated formic acid (85%), 50% of (V) with a b. p. of 80-82° (1 mm), d_4^{20} 1.0065, n_D^{20} 1.5191 was obtained, and the remainder was a mixture of (V) and (VI). The same picture was observed on boiling (VI) with 60% formic acid. On boiling (VI) with sulfuric acid (1:3) for 2 hours a 60-80% yield of (V) was obtained. (b. p. 103-106° at 17 mm, n_D^{20} 1.5191).

On reaction of 30 g of the alcohol (VI) with 100 ml of sulfuric acid (1:3) in the cold, with stirring, for 40 hours, 22 g (80%) of the tetrahydrofuran (V) with a b. p. of 103° (10 mm), n_D^{20} 1.5190 was isolated, but on stirring 40 g of the unsaturated alcohol (VI), with a b. p. of 145.5° (12 mm), in the cold for 33 hours with 150 ml of sulfuric acid (pH 1.6), 35 g of the alcohol with a b. p. of 144-145° (11 mm), n_D^{20} 1.5600 was recovered.

SUMMARY

1. The dehydration of two primary-tertiary γ-glycols, 2-methylpentanediol-2,5 and 2-phenylpentanediol-2,5, was studied.

2. It was shown that on dehydration under mild conditions (acid with a pH of 1.6) we were able to isolate the intermediate dehydration product of the first glycol, the unsaturated primary alcohol, 2-methylpenten-2-ol-5, which, on distillation at atmospheric pressure, isomerized to 2,2-dimethyltetrahydrofuran.

3. It was found that 2-phenylpenten-2-ol-5 did not isomerize to the tetrahydrofuran derivative, but under severe conditions was converted to it by hydration, followed by dehydration of the glycol which formed.

4. The dehydration of 2-phenylpentanediol-2,5 took place with the formation of water due to the two hydroxyl groups; we were unable to obtain from it the unsaturated alcohol, 2-phenylpenten-2-ol-5; 2-2-methylphenyltetrahydrofuran formed at once.

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SYNTHESIS AND TRANSFORMATION OF ETHYLENE α-GLYCOLS

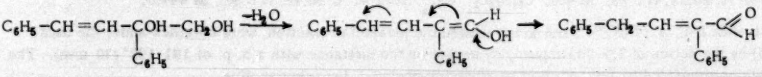
IV. 2,4-DIPHENYLBUTENE-3-DIOL-1,2

L. F. Chelpanova and V. A. Kormer

Earlier we found [1] that ethylene series ditertiary α-glycols, under the influence of 20% alcoholic sulfuric acid, undergo the pinacol rearrangement. It was of interest to find out what would result from an ethylene series primary-tertiary α-glycol under the same conditions.

One of us [2] obtained 2,4-diphenylbutene-3-diol-1,2 by hydrogenation of the appropriate acetylene glycol in the presence of colloidal palladium. The isomer with a m. p. of 52-53° was used for the present study. It was heated at 50° with a 14% alcoholic solution of H_2SO_4. Under these conditions, 30% (based on the starting material) of a bright-yellow, pleasant smelling, oily substance and 70% of a non-distilling solid, brown resin were isolated from the acid solution. The oily substance had the empirical formula $C_{16}H_{14}O$, showed a negative reaction for hydroxyl, instantly decolorized an aqueous solution of potassium permanganate, and relatively slowly decolorized bromine water, gave a rose coloration with fuchsin sulfurous acid, and gave a gray precipitate with an ammoniacal solution of silver oxide. With 2,4-dinitrophenylhydrazine, a red substance was obtained, which had a positive pyrazoline reaction. Phenylacetic and benzoylformic acids were formed by oxidation of the resulting substance in the cold with an aqueous solution of potassium permanganate.

These data enabled us to attribute to this substance the α,γ-diphenylcrotonaldehyde structure, which may be formed according to the scheme:



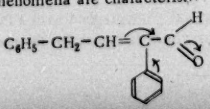
(a) (I)

The dehydration of the α-glycol and the formation of the enol (a) as the intermediate product which, being an unstable compound, rearranges to its isomeric α,γ-diphenylcrotonaldehyde (I), obviously occurs with the action of H_2SO_4.

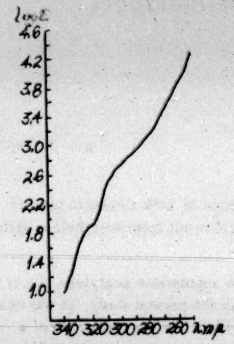
A partial transfer of a proton to the α-position to the resulting carbonyl group is possible, which leads to the formation of α,γ-diphenylvinylacetaldehyde (2,4-diphenylbuten-3-al)(II).

(II)

Yet the formation of this compound is energetically less profitable than the addition of a proton in the γ-position, which leads to the formation of α,γ-diphenylcrotonaldehyde, since in the latter instance we have a system with conjugated double bonds [3]. In our case this tendency for the formation of conjugated bonds also determined the direction of the reaction. α, γ-Diphenylcrotonaldehyde is mentioned only in the patent literature [4]. The boiling point cited for it agrees well with our value. The aldehyde has extremely curious optical properties: it produces no exaltation of the molecular refraction, in spite of the presence of conjugated double bonds in the molecule; its ultraviolet absorption curve had no characteristic maximum for the ketone carbonyl group [5] (Figure). These interesting phenomena are, apparently, explained by the presence in the α,γ-diphenylcrotonaldehyde of a disruption of the conjugation, of which these phenomena are characteristic



α, γ-Diphenylcrotonaldehyde, on standing in the air for 2 months, was converted almost completely to a white crystalline substance, which was insoluble in ether, alcohol, hexane, and benzene. The substance had the empirical formula $C_{16}H_{14}O_2$, decolorized bromine water, decolorized an aqueous solution of potassium permanganate, and was characterized as α,γ-diphenylcrotonic acid.



Ultraviolet absorption curve of α,γ-diphenylcrotonaldehyde.

The brown resin obtained in the residue after distillation had the empirical formula $C_{32}H_{28}O_2$, gave negative reactions for hydroxyl and for carbonyl (with 2,4-dinitrophenylhydrazine), and decolorized neither an aqueous solution of potassium permanganate nor bromine water. The ultraviolet absorption curve had neither maxima nor minima, and proved to be identical with the absorption curve of α,γ-diphenylcrotonaldehyde (Figure).

The oxidation, carried out with an aqueous solution of potassium permanganate at the boiling point of the bath, gave not the slightest positive results. The data of the elementary analysis enabled us to assume the formation of an α,γ-diphenylcrotonaldehyde dimer. We were unable to establish the structure of the dimer.

EXPERIMENTAL

18 g of the ethylene glycol (m. p. 52-53°) was heated with a 14% alcoholic solution of H_2SO_4 at 50° for 3 hours. On completion of the heating the mixture was diluted with cold water and was extracted with ether. A bright-yellow, oily substance with a b. p. of 191-192° (10 mm), and with a pleasant odor, was distilled from the residue after removal of the ether.

d_4^{20} 1.1017, n_D^{20} 1.6065, MR_D 69.50; calc. 69.50

Found %: C 86.22; H 6.30. M 221.0. $C_{16}H_{14}O$. Calculated %: C 86.48; H 6.30. M 222.0.

The residue after distillation was a solid, brown resin which, according to analytical data, corresponded to the aldehyde dimer.

Found %: C 86.22; H 6.29. M 450. $C_{32}H_{28}O_2$. Calculated %: C 86.48; H 6.30. M 444.0.

Crystals with a m. p. of 52-54°, and which showed the pyrazoline reaction, were obtained under the usual conditions [6] by the action of 2,4-dinitrophenylhydrazine on the substance with a b. p. of 191-192° (10 mm). The analytical data corresponded to 1-(2',4'-dinitro)-phenyl-4-phenyl-5-benzylpyrazoline.

Found %: N 13.81. $C_{22}H_{18}O_4N_4$. Calculated %: N 13.09.

Oxidation of the substance with a b. p. of 191-192° (10 mm). 2 g of the aldehyde was placed in a flask with a mechanical stirrer and a reflux condenser, and 125 ml of 2% potassium permanganate was added dropwise during 12 hours, in the cold. On the next day, after separation of the acid and neutral products, a small quantity of starting material was found. The salts of the acids were partially evaporated. Phenylacetic acid crystals with a m. p. of 75-76° precipitated on acidification. A test of a mixture with known phenylacetic acid gave no depression [7]. Benzoylformic acid, which gave a positive reaction with phenylhydrazine [8], formed from the filtrate; its silver salt was obtained.

Found %: Ag 41.95. $C_8H_5O_3Ag$. Calculated %: Ag 42.02.

The substance with a b. p. of 191-192° (10 mm), after standing for 2 months, was converted to white crystals with a m. p. of 224-225° (from a mixture of toluene and xylol), and which did not dissolve in alcohol, ether, benzene or hexane. The resulting substance had an acid reaction.

Found %: C 80.30, 80.52; H 5.50, 5.42. $C_{16}H_{14}O_2$. Calculated %: C 80.67; H 5.88.

The acid was converted to the silver salt.

Found %: Ag 31.60. $C_{16}H_{13}O_2Ag$. Calculated %: Ag 31.30.

Absorption Spectra

The ultraviolet absorption spectrum was photographed with a PSP-22 quartz spectrograph. A "Banner" factory hydrogen lamp served as the source of ultraviolet radiation for the continuous spectrum. A cuvette of variable depth

with a maximum depth of 10 mm was used for exposure of the spectrum. Hexane solutions of 0.015 and 0.0005 M concentrations were studied. The wavelengths in the absorption spectrum were determined by the arc spectrum of iron photographed on the same sheet. The method of equal blackening was used for the photometry.

SUMMARY

Upon action of a 14% alcoholic solution of sulfuric acid on 2,4-diphenylbutene-3-diol-1,2, a dehydration of the glycol with the formation of α,γ-diphenylcrotonaldehyde takes place.

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TRANSFORMATION OF ACETYLENE γ-GLYCOLS

V. ISOMERIZATION OF ASYMM. -DIMETHYL-DI-p-TOLYLBUTYNEDIOL (2-METHYL-5,5-p-TOLYLPENTYNE-3-DIOL-2,5)

E. D. Venus-Danilova and Z. V. Printseva

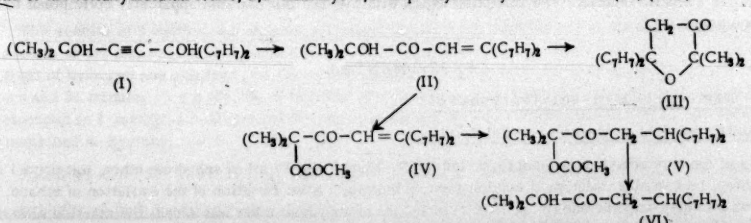
The intramolecular transformations of acetylene series ditertiary γ-glycols, unlike their hydrogenation, have been studied in a relatively small number of instances.

It is known from the literature that tetramethylbutynediol and its homologs, on heating with dilute solutions of mercury salts, form substituted β-ketohydrofurans [1]; tetramethylbutynediol, with mercury acetate in acetic acid in the presence of boron fluoride, cyclizes to 2,2,5,5-tetramethyltetrahydro-3-ketofuran [2]; under the influence of sulfuric acid, tetrapropylbutynediol and symm. dimethyldiamylbutynediol isomerize to 2,2,5,5-tetrapropyltetrahydro-3-ketofuran and 2,5-dimethyl-2,5-diamyltetrahydro-3-ketofuran [3].

Studying the transformations of asymm.-dimethyldiphenylbutynediol under relatively mild conditions (alcoholic solution of sulfuric acid of different concentrations with gentle heating), one of us and V. I. Ryabtseva and L. A. Grigoryeva [4] showed that this glycol isomerizes to ethylene α-keto alcohol, which with an increase of the acid concentration cyclizes to tetrahydrofuranone.

In order to confirm this observation, we studied the transformations of asymm. dimethyl-di-p-tolylbutynediol under similar conditions.

Dimethyl-di-p-tolylbutynediol (I), synthesized via the organomagnesium compound from dimethylacetylenecarbinol and di-p-tolyl ketone, by the action of a 7.5% alcoholic solution of sulfuric acid at 30-35° formed two isomerization products: the ethylenic α-keto alcohol, 2-methyl-5,5-di-p-tolylpenten-4-ol-2-one-3 (II) and a ketone of the tetrahydrofuran series, 2,2-dimethyl-5,5-di-p-tolyltetrahydrofuranone-3 (III) (30%).

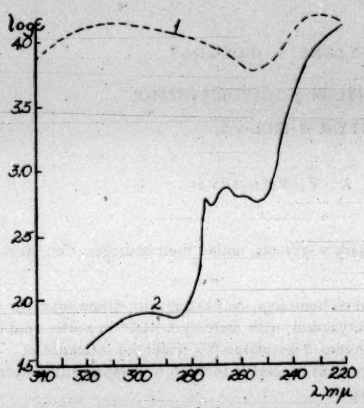


It should be noted that 2-methyl-5,5-di-p-tolylpenten-4-ol-2-one-3 (II) cyclized to tetrahydrofuranone (III) more readily than did the corresponding ethylenic α-keto alcohol described in the preceding report [4]. By the action of a 7.5% alcoholic solution of sulfuric acid on the glycol (I), together with the unsaturated α-keto alcohol (II), the tetrahydrofuranone (III) (30%) was also observed. This was not observed on isomerization of the asymm. dimethyldiphenylbutynediol. The large negative charge of the CH-group of the p-tolyl keto alcohol (II), caused by the presence of the methyl group in the para-position of the benzene nucleus, compared with the keto alcohol with phenyl radicals, apparently facilitates cyclization.

The 2,4-dinitrophenylhydrazone and the unsaturated acetate, 2-methyl-5,5-di-p-tolyl-2-acetoxypenten-4-ol-2-one-3 (IV), were obtained for the unsaturated α-keto alcohol. The structure of the unsaturated keto alcohol (II) was demonstrated by obtaining α-hydroxyisobutyric acid and di-p-tolyl ketone by ozonization.

The ethylenic α-keto alcohol (II) hydrogenated completely neither in the presence of colloidal palladium, nor in the presence of platinum black; we also encountered a difficult hydrogenation for the ethylenic keto alcohol

with phenyl radicals [4], although we were able to obtain the corresponding saturated keto alcohol, 2-methyl-5,5-diphenyl pentanol-2-one-3 from it.



Ultraviolet spectra in alcohol.
1) 2-Methyl-5,5-di-p-tolylpenten-4-ol-2-one-3;
2) 2,2-dimethyl-5,5-di-p-tolyltetrahydrofuranone-3.

The acetate of 2-methyl-5,5-di-p-tolylpenten-4-ol-2-one-3 (IV), obtained by the usual method by heating the ketol with acetic anhydride in the presence of sodium acetate, was reduced to the saturated acetate, 2-methyl-5,5-di-p-tolyl-2-acetoxypentanone-3 (V), by catalytic hydrogenation in the presence of platinum. On hydrolysis with alcoholic alkali the acetate gave the saturated α-keto alcohol, 2-methyl-5,5-di-p-tolylpentanol-2-one-3 (VI).

Only 2,2-dimethyl-5,5-di-p-tolyltetrahydrofuranone-3 (III) was obtained by the action of 18% sulfuric acid on asymm.-dimethyl-di-p-tolylbutynediol (I). This same ketone was also formed under similar conditions from the unsaturated ethylenic α-keto alcohol (II).

The absorption curves of alcoholic solutions of 2-methyl-5,5-di-p-tolylpenten-4-ol-2-one-3 (II) and 2,2-dimethyl-5,5-di-p-tolyltetrahydrofuranone-3 (III) in the ultraviolet part of the spectrum • are presented in the Figure.

Curve 1 resembles the curves corresponding to the absorption curve of 2-methyl-5,5-diphenylpenten-4-ol-2-one-3 and 2-methyl-5-phenylpenten-4-ol-2-one-3, presented in the preceding report [4]. Also, in the present case, for the ethylenic α-keto alcohol (II), an elevated absorption intensity characteristic of compounds containing an aromatic nucleus in conjugation with C=C or C=O-groups, and a displacement of the ketonic group maximum toward the long-wave part of the spectrum [5] ($\lambda_{max.}$ 310 mμ, ε 14169), were observed.

Curve 2, corresponding to the substituted furanone, had an entirely different character. The carbonyl group absorption maximum shifted somewhat toward the long-wave part of the spectrum ($\lambda_{max.}$ 297 mμ, ε 79.9) under the influence of the aromatic radicals. The absorption region with 240-280 mμ maxima apparently corresponds to isolated tolyl groups [5].

EXPERIMENTAL

Asymm.-Dimethyl-di-p-tolylbutynediol

(2-Methyl-5,5-di-p-tolylpentyne-3-diol-2,5) (I)

17.5 g of dimethylacetylenecarbinol (b. p. 100-103°), diluted with 50 ml of anhydrous ether, was poured slowly, with stirring, into an ether solution of ethylmagnesium bromide. After cessation of the evolution of ethane, a solution of 43 g of di-p-tolyl ketone (m. p. 93-94°) in 100 ml of anhydrous ether was added; the reaction substance was heated on the water bath at 60-70° for 70 hours with vigorous stirring, and was decomposed with water and ice and with dilute sulfuric acid. 42 g (70%) of colorless crystals, which melted at 115-116° (from gasoline), were isolated from the ether extract. The glycol was highly soluble in alcohol and in ether, but less soluble in benzene and gasoline. Acetylene, characterized by silver acetylide, was formed by cleavage with potash [6].

Found %: C 81.80, 81.70; H 7.40, 7.50; OH 11.32, 11.59. M 303. $C_{20}H_{20}(OH)_2$. Calculated %: C 81.63; H 7.48; OH 11.56. M 294.

2-Methyl-5,5-di-p-tolylpenten-4-ol-2-one-3 (II)

The transformation of asymm.-dimethyl-di-p-tolylbutynediol (I) (10 g) was carried out by heating in the presence of 7.5% alcoholic sulfuric acid (80 ml) at about 30-35° for 6 hours. After cooling, fine, bright-green crystals precipitated from the solution. The same substance was extracted by ether from the solution diluted with water.

• The spectra were measured with an SF-4 spectrophotometer by U. A. Dranitsinaya, for which we thank her.

4.8 g (48%) of bright greenish-yellow crystals with a m. p. of 127° which were highly soluble in organic solvents, was obtained after recrystallization from low-boiling gasoline. The substance decolorized an aqueous solution of potassium permanganate, a solution of bromine in chloroform, and gave a positive reaction for hydroxyl and carbonyl groups.

After 3 days, after separation of the bright greenish-yellow crystals with a m. p. of 127° from the mother liquor, 3 g (30%) of large, colorless crystals precipitated, which, after recrystallization from alcohol, had a m. p. of 65-66° and, as further experiments showed, corresponded to the substituted tetrahydro-β-furanone (III). An analysis of the substance with a m. p. of 127° is presented below.

Found %: C 81.48, 81.47; H 7.76, 7.60; OH 6.19, 5.75. M 308. $C_{20}H_{21}O(OH)$. Calculated %: C 81.63; H 7.48; OH 5.78. M 294.

A bright-red precipitate with a m. p. of 191-192° (from alcohol), which gave the pyrazoline reaction, came down at once on reaction of the substance with 2,4-dinitrophenylhydrazine [7].

Found %: C 65.66; H 5.74; N 12.19, 12.05. $C_{26}H_{26}O_5N_4$. Calculated %: C 65.82; H 5.49; N 11.81.

The analytical data corresponded to the ethylenic α-keto alcohol, 2-methyl-5,5-di-p-tolylpenten-4-ol-2-one-3 (II).

The ozonization of the substance (2.5 g) was carried out in chloroform (45 ml). 0.54 g of ozone was absorbed after 65 minutes (the theoretical quantity was 0.41 g). After the usual decomposition of the ozonide and separation of the neutral and acid products, 1.4 g (78%) of di-p-tolyl ketone with a m. p. of 93-95° (from alcohol) was obtained, which gave no melting point depression with aknown preparation of the ketone, and a small quantity of acetone, demonstrated by the 2,4-dinitrophenylhydrazone, was obtained. 0.7 g (79 %) of α-hydroxyisobutyric acid with a m. p. of 76-78°, which gave no depression with known α-hydroxyisobutyric acid, and a negligible quantity of p-toluic acid, were isolated from the acid products.

The acetate of 2-methyl-5,5-di-p-tolylpenten-4-ol-2-one-3 (IV) was obtained by the usual method, by heating 2.5 g of the unsaturated keto alcohol (II) with 8 ml of freshly-distilled acetic anhydride in the presence of 2 g of sodium acetate. The resulting acetic ester, 2-methyl-5,5-di-p-tolyl-2-acetoxypenten-4-one-3 (IV), decolorized an aqueous solution of potassium permanganate, but gave no hydroxyl group reactions. In spite of repeated recrystallization from different solvents, we were unable to obtain a definite melting point for the substance. It melted at 90-94°.

Found %: C 78.10; H 7.20. M 345. $C_{22}H_{24}O_3$. Calculated %: C 78.57; H 7.14. M 336.

The acetate of 2-methyl-5,5-di-p-tolylpentanol-2-one-3 (V) was obtained by the hydrogenation of 1.2 g of the acetate of the unsaturated keto alcohol (IV) in 50 ml of ethyl acetate in the presence of 0.4 g of platinum black. 101.8 ml of hydrogen was absorbed (the theoretical quantity was 85.6 ml at the same temperature and pressure) after 4 hours and 25 minutes. 0.8 g (66.7%) of colorless crystals with a m. p. of 97-98° (from alcohol) was isolated, which corresponded to 2-methyl-5,5-di-p-tolyl-2-acetoxypentanone-3 (V). The substance exhibited saturated properties and contained no hydroxyl.

Found %: C 77.85, 77.97; H 7.49, 7.98. M 346. $C_{22}H_{26}O_3$. Calculated %: C 78.11; H 7.69. M 338.

2-Methyl-5,5-di-p-tolylpentanol-2-one-3 (VI) was synthesized by the hydrolysis of 0.7 g of the acetate (V) by alcoholic potassium hydroxide. 0.51 g (83%) of a colorless, crystalline substance was isolated, which was very highly soluble in all organic solvents and which, after washing on the filter with a very small quantity of cold alcohol, melted at 62°. The reaction for carbonyl and hydroxyl groups was positive.

Found %: C 80.76; H 8.53; OH 5.78, 6.20. M 294. $C_{20}H_{23}O(OH)$. Calculated %: C 81.08; H 8.81; OH 5.74. M 296.

The semicarbazone was obtained by the usual method with gentle heating. After recrystallization from alcohol its m. p. was 115°.

Found %: N 12.00. $C_{21}H_{27}O_2N_3$. Calculated %: N 11.89.

The 2,4-dinitrophenylhydrazone was obtained by Shriner and Fuson's procedure [7]. It consisted of orange-yellow crystals with a m. p. of 146° (from a mixture of alcohol and ethyl acetate).

Found %: N 11.41. $C_{26}H_{26}O_5N_4$. Calculated %: N 11.76.

2,2-Dimethyl-5,5-di-p-tolyltetrahydrofuranone-3 (III)

Transformation of asymm.-dimethyl-di-p-tolylbutynediol (I) in the presence of 18% sulfuric acid. 5 g of acetylene glycol (m. p. 115-116°) was heated (water bath) with 40 ml of 18% alcoholic sulfuric acid at 60-70° for 7.5 hours. On the next day, 2.7 g of colorless crystals with a m. p. of 65-66° was precipitated from the solution; on dilution of the filtrate with water and on neutralization with soda, 1.5 g more of the crystals which also melted at 65-66° (from alcohol) was extracted with ether.

The substance contained no hydroxyl groups, did not decolorize potassium permanganate and bromine solutions, and was identical to the substance obtained along with the ethylenic α-keto alcohol by the action of a 75% alcoholic solution of sulfuric acid on the acetylene glycol, and corresponded to 2,2-dimethyl-5,5-di-p-tolyltetrahydrofuranone-3 (III). Its yield was 84%.

Found %: C 81.44, 81.47; H 7.57, 7.40. M 304 8, 301.3. $C_{20}H_{22}O_2$. Calculated %: C 81.63; H 7.48. M 294.

The 2,4-dinitrophenylhydrazone was obtained by the usual method. It precipitated quickly as yellow crystals with a m. p. of 193-194° (from a mixture of alcohol and ethyl acetate).

Found %: C 65.67; H 5.88; N 11.43. $C_{26}H_{26}O_5N_4$. Calculated %: C 65.82; H 5.49; N 11.81.

The semicarbazone was obtained after prolonged heating by boiling an alcoholic solution of the tetrahydrofuranone with a semicarbazide solution. After recrystallization from alcohol its m. p. was 288° (decompn.).

Found %: C 71.96, 72.02; H 6.71, 6.63; N 12.06, 11.89. $C_{21}H_{25}O_2N_3$. Calculated %: C 71.79; H 7.10; N 11.97.

The isomerization of 2-methyl-5,5-di-p-tolylpenten-4-ol-2-one-3 was carried out by heating 1 g of the ethylenic α-keto alcohol (II) with 16 ml of an 18% alcoholic solution of sulfuric acid at about 60-70°, during which the original greenish-yellow color of the solution gradually disappeared. After cooling, the reaction mixture was diluted with water, and the sulfuric acid was neutralized with soda. From the ether extract, after recrystallization from alcohol, 0.6 g (60%) of colorless crystals with a m. p. of 66° was obtained, which gave no melting point lowering with tetrahydrofuranone (III). The resulting 2,4-dinitrophenylhydrazone (m. p. 193-194°) corresponded to the 2,4-dinitrophenylhydrazone of 2,2-dimethyl-5,5-di-p-tolyltetrahydrofuranone-3 (III).

SUMMARY

1. Asymm.-dimethyl-di-p-tolylbutynediol (2-methyl-5,5-di-p-tolylpentyne-3-diol-2,5) was synthesized and it was shown that, in the presence of an alcoholic solution of sulfuric acid, this glycol isomerized to the ethylenic α-keto alcohol, 2-methyl-5,5-di-p-tolylpenten-4-ol-2-one-3 (7.5% acid) and to the tetrahydrofuran series cyclic ketone, 2,2-dimethyl-5,5-di-p-tolyltetrahydrofuranone-3 (18% acid).

2. The derivatives of the compounds synthesized were described. All the substances mentioned were obtained for the first time.

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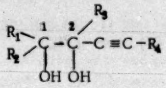
INVESTIGATION OF THE TRANSFORMATIONS OF PRIMARY-TERTIARY GLYCOLS OF THE ACETYLENE SERIES

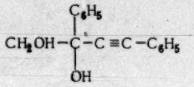
I. TRANSFORMATIONS OF PHENYL-PHENYLACETYLENYL-ETHYLENE GLYCOL (2,4-DIPHENYLBUTYNE-3-DIOL-1,2)

L. A. Pavlova

An investigation of the transformations of acetylene series ditertiary α-glycols (I) showed that in an acid medium these compounds are capable of changing in two directions, undergoing the acetyline-allene and the pinacol rearrangements. It was also found that the relative quantities of both reaction products depend on the structure of the glycols, i. e., on the nature of the R_1, R_2, R_3 and R_4 radicals and on their mutual arrangements [1]:



(I)



(II)

A study of primary-tertiary glycols, for which $R_1 = R_2 = H$, must supplement these investigations and show how the hydrogen atoms attached to the first hydroxylated carbon atom affect the nature of the rearrangement of the glycol.

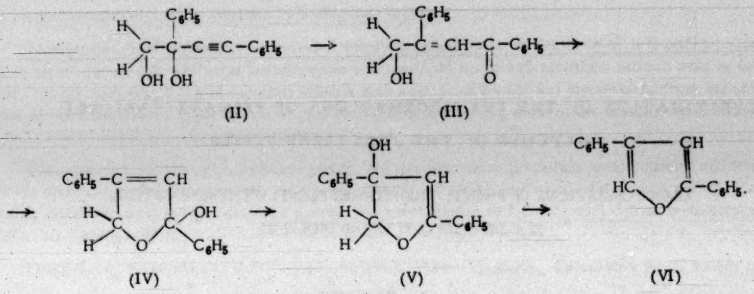
Phenyl-phenylacetylenyl-ethylene glycol (2,4-diphenylbutyne-3-diol-1,2) (II) was chosen as an example of an acetylene series primary-tertiary glycol.

The glycol, synthesized from benzoylcarbinol and phenylacetylene by Iotsich's method, was treated with an aqueous solution of sulfuric acid under different conditions: acid of different concentration 30, 20, 10% was used; the reaction mixture was heated at 60, 80° and on a boiling water bath; some experiments were carried out in a carbon dioxide atmosphere; in a series of experiments dioxane was added for homogenization of the mixture. In all the experiments, as a result of the reaction, a caramel-like substance of a more or less reddish-brown color was obtained, which displayed a hydroxyl group, decolorized a solution of potassium permanganate and of bromine water, was slightly colored by fuchsin sulfurous acid, and reduced silver oxide. From the resulting substance we were able to isolate a small quantity of a solid product, with a m. p. of 185-186°, which was poorly soluble in the usual organic solvents. Because of its small quantity, the substance was not closely studied. A treatment with an aqueous solution of oxalic acid led to the same results.

Similar data were obtained by E. D. Venus-Danilova and V. M. Albitskaya [2] by the action of sulfuric acid on the secondary-tertiary glycol, diphenyl-phenylacetylenyl-ethylene glycol. We were also unable to isolate the individual transformation products for this substance.

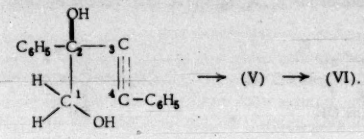
An alcoholic solution of mercuric chloride [2, 3] was used as the isomerizing agent in investigation of the transformations of the secondary-tertiary glycols; moreover, tri-substituted furans were formed, the formation of which was via the intermediate stage of the acetylene-allene rearrangement of the glycol.

The action of an alcoholic solution of mercuric chloride on the primary-tertiary glycols was also tested in the present work; moreover, a 65% yield of 2,4-diphenylfuran (VI) was obtained. Variation of the quantitative proportions of the glycol and the mercuric chloride (1 : 1 and 4 : 1) affected the furan yield little. It can be assumed that the formation of diphenylfuran from the glycol takes place via the acetylene-allene rearrangement stage according to the scheme proposed earlier for the secondary-tertiary glycol:



(II) (III) (IV) (V) (VI)

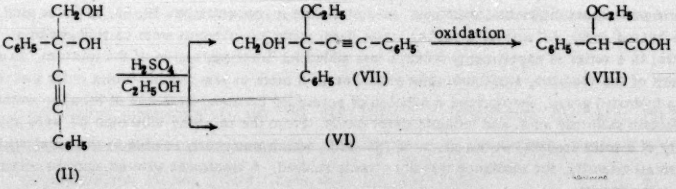
However, to us a different mechanism of the formation of 2,4-diphenylfuran from the glycol seems possible. At first the hydrogen of the hydroxyl group of the first carbon atom adds to the third carbon atom, and the fourth carbon atom combines with oxygen. A similar addition is possible as a result of the activation of the triple bond by the catalyst. The 2,4-diphenyl-4-hydroxydihydrofuran-4,5 (V) which forms at this time is dehydrated to 2,4-diphenylfuran (VI).



(II)

The data of our work did not permit us to make a choice between the schemes indicated.

We also studied the action of an alcoholic solution of sulfuric acid on the glycol. In this case the reaction proceeded in two directions; the formation of the incomplete ether of the glycol, which was characterized as the 2-ethoxy-2,4-diphenylbutyn-3-ol-1 (VII) was the chief reaction direction, and 2,4-diphenylfuran (VI) formed according to the second reaction direction.



(II) (VI) (VII) (VIII)

In this reaction the formation of the ether by the tertiary hydroxyl agrees with the literature. It is known that tertiary alcohols form ethers more readily than do primary alcohols. Alcohols containing aromatic radicals or radicals with multiple bonds form ethers with still greater ease [4].

EXPERIMENTAL

Phenyl-phenylacetylenyl-ethylene glycol (2,4-diphenylbutyne-3-diol-1,2) was obtained in a 65% yield from benzoylcarbinol and phenylacetylene by Iotsich's method. This compound was obtained for the first time by L. F. Chelpanova and N. M. Libman [5]. From a mixture of ethyl and petroleum ethers the glycol was obtained as fine, lustrous needles with a m. p of 106-107°, and not 101-102° as indicated in the literature.

Action of an Alcoholic Solution of Mercuric Chloride on Phenyl-phenylacetylenyl-ethylene Glycol

Experiment 1. 65 ml of ethyl alcohol was poured into a mixture of 5 g of the glycol and 5.6 g of mercuric chloride (1 mole of the glycol : 1 mole of mercuric chloride). On heating the reaction mixture the precipitate acquired a curdy form and the substance solidified. At a bath temperature of 80° a yellowing of the mixture began, which was intensified with the boiling of the alcohol. The precipitate gradually dissolved. After an hour of heating, the solution was cooled. On cooling, a yellow crystalline precipitate came down, which was separated from the solution and recrystallized from ligroin. 3 g of a product with a m. p. of 105-106° was obtained (65% yield based on diphenylfuran). The melting point of the substance increased to 109-110° with a second recrystallization. The purified product had the form of colorless scales with an unusual lilac-like fluorescence. The solution of the resulting substance in concentrated sulfuric acid showed a very strong red-blue fluorescence. On storage, the substance turned yellow.

From the alcoholic solution obtained after separation of the product with a m. p. of 109-110°, the alcohol was removed, and the residue was treated with benzene. The dissolving in benzene was partial. The insoluble residue amounted to 2.4 g. An analysis showed that this was mercuric chloride. After removal of the benzene from the benzene extract 1.5 g of a dark, viscous resin was obtained.

Experiment 2. 20 ml of ethyl alcohol was added to a mixture of 1.8 g of the glycol and 0.5 g of mercuric chloride (4 moles of the glycol; 1 mole of mercuric chloride), and the mixture was heated. No differences from Experiment 1 were observed. 0.75 g (45%) of a substance with a m. p. of 108-110° was isolated, which was identical to the product obtained in Experiment 1.

Found %: C 86.97; H 5.61. M 223. $C_{16}H_{12}O$. Calculated %: C 87.27; H 5.45. M 220.

According to its analytical data and properties, the substance with a m. p. of 109-110° corresponded to the 2,4-diphenylfuran described in the literature [6].

On heating with solvents and on standing of the solutions, the 2,4-diphenylfuran was partially converted to an amorphous powder, which greatly hampered the purification of this substance. This observation also agreed with the literature [6].

Action of an Alcoholic Solution of Sulfuric Acid on Phenyl-phenylacetylenyl-ethylene Glycol

11 g of the glycol was dissolved in 100 ml of a 12% solution of sulfuric acid in ethyl alcohol. The solution was heated on the water bath for 2 hours at 40-45°. In proportion to the heating, the reaction mixture turned yellow, and toward the end it turned slightly brown. The solution was cooled, diluted with water, and treated with ether. The ether extract was washed carefully with a soda solution and with water, and was dried with sodium sulfate. After removal of the ether 11.5 g of a brownish oil was obtained. 1.5 g of the resulting oily product was vacuum distilled. At 150° (1 mm) a partial decomposition was observed, and at 180-182° (1 mm) a faintly colored viscous liquid distilled, which solidified before long.

On standing, the non-distilled oil (10 g) began to crystallize shortly. On recrystallization of the resulting precipitate from petroleum ether, a substance with a m. p. of 69-70° was obtained, which was identical to the product obtained by distillation. In all, 6.6 g was isolated (53.6% on the basis of the incomplete ethyl ether of the glycol). The oily product which remained after separation of the precipitate was mixed with alcohol and heated to boiling. The crystals which precipitated on cooling of the solution were filtered off and recrystallized from ligroin. 1.5 g (14.5%) of a substance with a m. p. of 109° was obtained, which gave no melting point depression in a mixture with 2,4-diphenylfuran.

By the action on the glycol of a 17% solution of sulfuric acid in alcohol at room temperature for 15 minutes, the glycol did not change, but a 2.5-hour treatment of the glycol under these same conditions gave an 83% yield of a substance with a m. p. of 66-68°, which was identical to the product obtained by the action of a 12% alcoholic solution of sulfuric acid.

The substance with a m. p. of 69-70°, and a b. p. of 180-182° (1 mm), was highly soluble in ethyl alcohol, acetone, benzene, ethyl acetate, and chloroform. It could be recrystallized from aqueous alcohol or petroleum ether. The substance gave no reactions for the carbonyl group, but hydroxyl and ethoxy-group were detected. No formation of phenylacetylene was observed on heating this product with freshly-calcined potash.

Found %: C 81.02, 81.00; H 6.91, 6.90; OH 7.5; OC_2H_5 17.00. M 259. $C_{16}H_{12}(OH)(OC_2H_5)$. Calculated %: C 81.20; H 6.77; OH 6.4; OC_2H_5 16.91. M 266.

The analytical data corresponded to the incomplete ethyl ether of the glycol.

The oxidation of the incomplete ethyl ether of the glycol in a quantity of 3 g was carried out by shaking with an aqueous solution of potassium permanganate (3 g of the salt, 300 ml of water) at room temperature. 4 hours after oxidation of the mixture began, 3 g more of potassium permanganate was added as a powder in small portions during 3 hours. Since complete decolorization was not attained after 7 hours of oxidation, 50 ml of pyridine was added to the mixture, and the reaction substance was heated at about 40-45° for 1 hour, with stirring.

In order to separate the neutral oxidation product the manganese dioxide was filtered off, and washed with warm water and with ether. From the filtrate and wash water, with some discharging, the volatile-with-steam products and pyridine were distilled. In the distillate the pyridine was combined with the calculated quantity of dilute sulfuric acid, and after this the neutral products were extracted with ether. On removal of the ether 0.4 g of a substance was obtained, which melted at 63-65° and gave no melting point depression with the original product. No neutral oxidation products non-volatile with steam were observed. The solution of the salts of the organic acids was concentrated on the water bath. On decomposition of the salts by cold dilute sulfuric acid a solid white substance was separated, which, after recrystallization from hot water and drying, had a m. p. of 118-119° and gave no melting point depression in a mixture with benzoic acid. 1.1 g (~90%) of benzoic acid was obtained. The organic acids which remained were extracted with ether. After removal of the ether 1.6 g (~88%) of a liquid substance was obtained, from which the silver salt was obtained by the method of double decomposition. The silver salt was recrystallized from hot water and washed on the filter with ether. On storage in the solid form, the silver salt was stable, but the aqueous solutions darkened rapidly.

Found %: C 41.40, 41.50; H 4.26, 4.00; Ag 37.55, 37.35, 37.93. $C_{10}H_{11}O_3Ag$. Calculated %: C 41.86; H 3.83; Ag 37.63.

The data obtained corresponded to α-ethoxy-α-phenylacetic acid (VIII).

Thus, benzoic acid and α-ethoxy-α-phenylacetic acid was obtained as a result of the oxidation [7].

On the basis of the oxidation data, the 2-ethoxy-2,4-diphenylbutyn-3-ol-1 structure may be attributed to the substance with a m. p. of 69-70°.

We express sincere appreciation for the consultation of Prof. E. D. Venus-Danilova.

SUMMARY

1. 2,4-Diphenylfuran formed on the treatment of asymm.-phenyl-phenylacetylenyl-ethylene glycol with mercuric chloride in an alcoholic solution.

2. The action of an alcoholic solution of sulfuric acid on phenyl-phenylacetylenyl-ethylene glycol led to the formation of two products, the incomplete ethyl ether of the glycol, 2-ethoxy-2,4-diphenylbutyn-3-ol-1, and 2,4-diphenylfuran.

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TERTIARY TRIATOMIC ALCOHOLS OF THE ACETYLENE SERIES AND THEIR TRANSFORMATIONS

VIII. DEHYDRATION OF TERTIARY ETHYLENIC GLYCEROLS: 2,3,6-TRIMETHYL-HEPTENE-4-TRIOL-2,3,6; 3,4,7-TRIMETHYLOCTENE-5-TRIOL-3,4,7; 2-METHYL-5-(1-HYDROXYCYCLOHEXYL)-HEXENE-3-DIOL-2,5, AND 2,4-DI-(1-HYDROXYCYCLOHEXYL)-BUTENE-3-OI-2

V. I. Nikitin and I. M. Timofeeva

In a previous report [1] we showed that tertiary ethylenic glycerols may be readily synthesized by the hydrogenation of the corresponding acetylene series triatomic alcohols. It was of interest to find out how ethylenic glycerols behave under the dehydration reaction conditions.

As one of us and A. Kh. Khamatov showed [2], the acetylene series glycerols, on treatment with dehydrating agents, are capable of losing one molecule of water, which leads to the development of a double bond in the molecule, with the formation of an isopropenylacetylene series α-glycol. Moreover, to some extent a process which proceeds with the formation of a second molecule of water also takes place, as a result of which vinylisopropenylacetylene alcohol forms.

As is well known, the dehydration reaction may be accompanied not only by the elimination of water due to hydroxyl and hydrogen on adjacent carbon atoms, with the formation of ethylenic and dienic bonds, but may also lead to an intramolecular rearrangement. This depends on the chemical nature of both the hydroxyl-containing compound and the dehydrating agent, the reaction conditions, and such.

In the present work the action of 10% sulfuric acid on 2,3,6-trimethylheptene-4-triol-2,3,6 (I), 3,4,7-trimethyloctene-5-triol-3,4,7(II), 2-methyl-5-(1-hydroxycyclohexyl)-hexene-3-diol-2,5 (III) and 2,4-di-(1-hydroxycyclohexyl)-buten-3-ol-2 (IV) was studied. It was shown that in each case, as a result of the reaction, the original triol lost only one molecule of water, with the formation of a homogeneous product, the best yield of which (about 85%) was obtained by the use of 10% acid. With 5% sulfuric acid part of the initial product remained unaltered, but the use of a 15% or higher concentration of acid brought about resinification.

The resulting substance had an unsaturated character; it was capable of decolorizing a potassium permanganate solution, and on hydrogenation in the presence of platinum oxide 1 mole of hydrogen per 1 mole of the substance added. According to the elementary composition there were two oxygen atoms in the molecule of the re-formed compound, one of which had a hydroxyl character and was easily determined by the Chugaev-Tserevitinov method. With respect to the second oxygen atom, it, not being hydroxyl, also had no carbonyl character. Attempts to obtain the 2,4-dinitrophenylhydrazone or the semicarbazone of these substances proved to be futile. We were also unable to reduce this oxygen to hydroxyl by metallic sodium in an alcohol solution or via the organomagnesium compound.

All this, and also the value found for the molar refraction, compelled us to ascribe an ether character to the second oxygen atom. Hence, it followed that the formation of water from the ethylenic glycerol molecule proceeded due to the two hydroxyl groups, and was accompanied by the closing of the remaining portion of the molecule into a ring through the oxygen heteroatom. Instances of the formation of such compounds as a result of the action of dehydrating agents on some unsaturated alcohols and ketones have been quite widely described in the chemical literature.

Thus, in the works of A. E. Favorsky and E. D. Venus [3], and E. D. Venus-Danilova and her coworkers [4], it was shown that for the ditertiary α-glycols with substituted acetylene radicals, under the influence of sulfuric acid, two forms of transformations are possible, the acetylene-allene transformation followed by cyclization to the substituted hydroxydihydrofurans, and the pinacol transformation with the formation of the acetylene ketone. Both of these transformations often take place uniformly for certain acetylene α-glycols. The authors noted that the character of the rearrangements dependson the nature of the radicals and on their mutual arrangement in the initial pinacol molecule. Under the influence of mercury salts, acetylene series secondary-tertiary α-glycols isomerize to the substituted furans [5].

E. D. Venus-Danilova, V. I. Ryabtseva and L. A. Grigoryeva [6] showed that by treatment with an alcoholic solution of sulfuric acid, depending on its concentration, asymm.-dimethyldiphenylbutynediol isomerizes to the keto alcohol, which with an increase of the acid concentration cyclizes to tetrahydrofuranone. The tertiary vinylacetylenecarbinols, as I. N. Nazarov and his coworkers showed, on heating with dilute sulfuric acid in the presence of mercuric sulfate, isomerize to tetrahydro-γ-pyrans [7, 8]. I. N. Nazarov and I. V. Torgov obtained tetrahydrofuran [9] by the dehydration of vinylacetylene γ-glycol with potassium bisulfate. As shown by several investigators, acetylene γ-glycols, in the presence of mercury salts, hydrate to the keto glycols, which are then dehydrated to tetrahydro-β-furanones [10, 11]. Let us cite the work of Ruhemann, which showed that under the influence of Na-ethylate, the diketone having a triple bond cyclizes to the pyrone derivative [12]. Diekman [13] observed the transformation of mesityl-oxo-oxalic ester to the pyrone derivative under the influence of mineral acids.

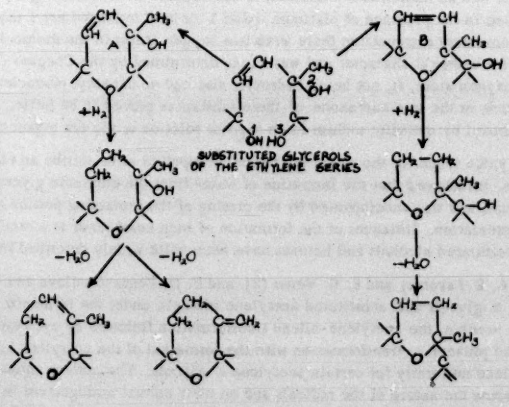
All that is stated above, and also the experimental data which we obtained, left no doubt of the heterocyclic character of the substances formed as a result of the dehydration of ethylene series tertiary triatomic alcohols. The ease with which the closure of the latter into the heterocyclic compound occurs indicated that all four of the ethylene series glycerols which we obtained were cis-forms and, consequently, that on hydrogenation of the acetylene glycerols over platinum oxide or over palladium precipitated on chalk no trans-form ethylenic glycerols formed at all [1]. However, depending on the fact that, due to any two hydroxyls the liberation of water from the ethylenic glycerols proceeds, here the formation of either the six-membered (A) (formation of H_2O from OH 1 and 3) or the five-membered heterocycle (B) (formation of H_2O from OH 1 and 2) may be expected.

Since it is impossible to establish a definite structure of these compounds by the method of oxidation, we carried out their catalytic hydrogenation in order to convert them by further dehydration to the unsaturated heterocyclic compounds (Scheme 1).

By the oxidation of the dehydration products we hoped to obtain data which would enable us to draw a more definite conclusion in favor of one or the other of their structures.

The heterocyclic compounds obtained as a result of the dehydration of all four of the ethylene series glycerols (I, II, III, IV) which we studied, were hydrogenated in the presence of a platinum catalyst. We consider it possible to ascribe to these heterocyclic compounds the substituted dihydropyranol structure, as will be shown below. They are 2,2,5,6,6-pentamethyldihydropyranol-5 (V); 2,2,5,6-tetramethyl-6-ethyldihydropyranol-5 (VI); 2,2,5-trimethyl-6-spirocyclohexanedihydropyranol-5 (VII) and 5-methyl-2,6-dispirocyclohexanedihydropyranol-5 (VIII). In their hydrogenation only 2 hydrogen atoms per 1 molecule of the hydrogenated substance were consumed, as a result of which the corresponding substituted tetrahydropyranols (IX, X, XI and XII) were isolated. One hydroxyl oxygen was easily determined in these latter by Chugaev-Tserevitinov's method, and the second oxygen had an ether character.

Scheme 1

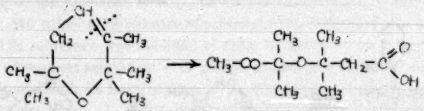


The dehydration of the tetrahydropyranols was carried out by their vacuum distillation in the presence of anhydrous potassium bisulfate. Only three of them (IX, X and XI) were dehydrated. Substituted dihydropyrans were obtained as a result of the dehydration of the tetrahydropyranols: 2,2,5,6,6-pentamethyl-Δ^4-dihydropyran (XIII); 2,2,5,6-tetramethyl-6-ethyl-Δ^4-dihydropyran (XIV) and 2,2,5-trimethyl-6-spirocyclohexane-Δ^4-dihydropyran (XV).

Pentamethyldihydropyran (XIII) and tetramethylethyldihydropyran (XIV) were oxidized with a 3% solution of potassium permanganate. Oxidation proceeded with great difficulty. Oxalic and acetic acids were obtained in both instances of oxidation; moreover, upon oxidation of pentamethyldihydropyran (XIII) a certain quantity of acid formed, the elementary analysis of which did not give completely satisfactory results, obviously because of the inadequate purity of the preparation. The molecular weight of this acid was determined from the quantity of alkali consumed by the titration and also from the percentage of barium in the salt. With great care we tried to find formic acid in the oxidation products; however, in not one case could even indications of its presence be detected. All these data gave no direct demonstration of the structure of the products which we studied; nevertheless, we considered these data adequate to indicate the greater probability of the pyran structure for the products. Moreover, we proceeded from the following assumptions: if the products of the dehydration of the ethylenic glycerols (I, II, III, IV) possessed the furan structure, then 2,3,6-trimethylheptene-4-triol-2,3,6 (I), after the reactions of dehydration, hydrogenation and dehydration again, which were carried out for it, would finally be converted to substituted isopropenyltetrahydrofuran, which on oxidation must give formic acid. We detected no traces of this acid in the oxidation products.

Furthermore, on oxidation we obtained an acid with a molecular weight close to 200. It seemed to us impossible to obtain an acid with such a high molecular weight by the oxidation of trimethylisopropenyltetrahydrofuran.

With respect to pentamethyldihydropyran (XIII), here it may seem that the oxidation may proceed at first only at the double bond, with the formation of the keto ether acid (XVI), the molecular weight of which equals 202, and this acid may be present in the oxidation products if only for a certain time, while no secondary oxidizing processes occur.



(XIII) (XVI)

We also think that of the two pyran structures possible, namely, the dihydropyran and tetrahydropyran structures with a heptacyclic bond, it is necessary to accept the dihydropyran structure. This assumption indicated the absence of formic acid in the oxidation products, which would have to give the methylene group-substituted tetrahydropyran.

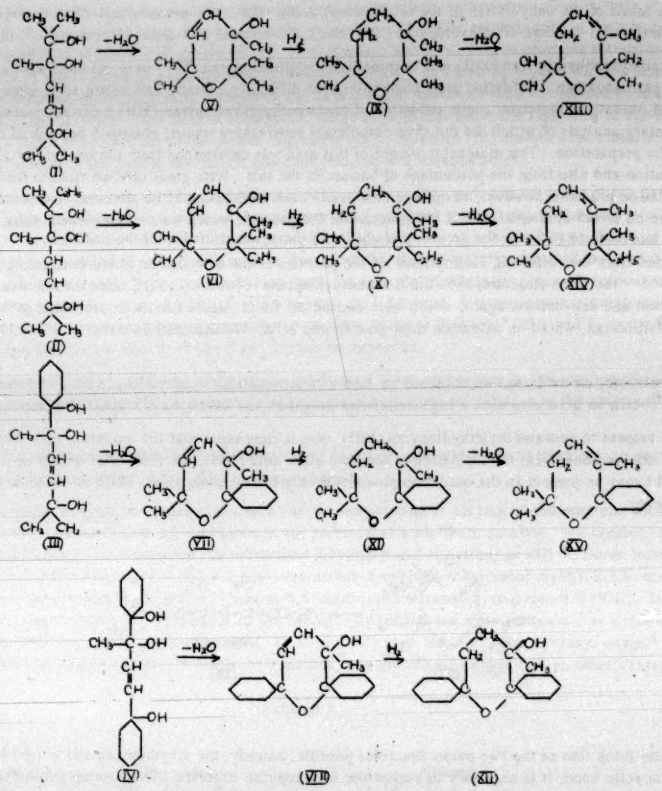
Furthermore, the dehydration of pentamethyltetrahydropyranol (IX) to the substituted tetrahydropyran with a heptacyclic bond, and not to the dihydropyran (XIII), would contradict the Wagner-Zaitsev rule. True, the dehydration sometimes does go counter to this rule; for example, when the less hydrogenated carbon atom is attached to an unsaturated radical [14]; however, this condition is absent here. Finally, in the oxidation of the substituted tetrahydropyran with the heptacyclic bond, we would sooner expect malonic acid than the oxalic acid which we isolated.

All that has just been stated also could be carried out for a chain of transformations, which we carried out for 3,4,7-trimethyloctene-5-triol-3,4,7, which also would favor the pyran structures of the products of these transformations.

The investigations of the transformations of ethylenic glycerols containing cyclohexyl radicals (III and IV) were not completed. However, we did not see the necessity of giving these transformations some other scheme, different from that which we proposed for the transformations of trimethylheptene- and trimethyloctenetriols.

On the basis of all that has been indicated above, we think it logical to assume Scheme 2 for the transformations which we carried out.

Scheme 2



EXPERIMENTAL

2,3,6-Trimethylheptene-4-triol-2,3,6 (I)

The triol was prepared by the hydrogenation of 2,3,6-trimethylheptyne-4-triol-2,3,6 [1], and had a m. p. of 116-117°.

Dehydration of 2,3,6-trimethylheptene-4-triol-2,3,6. 360 ml of 10% sulfuric acid was added to 15 g of the triol. The reaction was carried out at a temperature of 50-60°, with stirring, for 4 hours. A yellow, oily film separated from the emulsions which at first formed on the surface of the reaction mixture; the film became larger, and toward the end became considerable. The film was separated, and the aqueous residue was salted out with $(NH_4)_2SO_4$, and extracted with ether. The extract was combined with the oily layer, treated with a soda solution, washed with water, and dried with potash. The ether was removed, and from the remaining reaction products (14 g) 11.5 g (85%) of a fraction with a b. p. of 117-118° (8 mm) was distilled, which should be considered 2,2,5,6,6-pentamethyldihydropyranol-5 (V), which was not described in the literature.

d_4^{20} 0.9428, n_D^{20} 1.4507. MR_D 48.52. $C_{10}H_{18}O_2$. calc. 48.88.

Found %: C 70.35, 70.30; H 10.79, 10.70; OH 9.29, 9.89. $C_{10}H_{18}O_2$. Calculated %: C 70.58; H 10.60; OH 10.0.

Neither a 2,4-dinitrophenylhydrazone nor a semicarbazone formed.

Hydrogenation of 2,2,5,6,6-pentamethyldihydropyranol-5 (V). 7.1 g of the substance in 80 ml of methanol, distilled over alkali hydroxides, was hydrogenated over platinum oxide (according to Adams). 1106 ml of hydrogen (23°, 694.6 mm), calculated for one double bond, was absorbed. After this the reaction had practically ceased. The catalyst was filtered off, the product which remained was dried with potash and was then vacuum distilled. 6 g of 2,2,5,6,6-pentamethyltetrahydropyranol-5 (IX), which was not described in the literature, was isolated:

B. p. 59° (8 mm), d_4^{20} 0.9267, n_D^{20} 1.4404, MR_D 48.99. $C_{10}H_{20}O_2$. Calc. 49.34.

Found %: C 69.70; H 11.80; OH 9.76. $C_{10}H_{20}O_2$. Calculated %: C 69.76; H 11.60; OH 9.88.

We also were unable to obtain the 2,4-dinitrophenylhydrazone or the semicarbazone.

By treatment of a solution of 4 g of the substance in 20 ml of anhydrous ether with 12 g of methylmagnesium iodide, after a suitable treatment of the reaction products, the substance used in the reaction was recovered unaltered, which indicated the absence of the keto group.

Dehydration of 2,2,5,6,6-pentamethyltetrahydropyranol-5 (IX) with potassium bisulfate. 13 g of the substance, 4 g of finely-ground anhydrous potassium bisulfate and 0.5 g of pyrogallol were used. The reaction was carried out under ordinary pressure. At a bath temperature of 215° the reaction products with a b. p. of 140-150° distilled. 10.8 g of the crude products was obtained, which after drying with potash was distilled at 131 mm. Two fractions were obtained, the 1st, up to 86°, 5.5 g, n_D^{20} 1.4360; and the 2nd, 86-100°, 2.3 g, n_D^{20} 1.4400 (starting material).

The 1st fraction was the previously unknown 2,2,5,6,6-pentamethyl-Δ^4-dihydropyran:

B. p. 79-80° (70 mm), d_4^{20} 0.8549, n_D^{20} 1.4360, MR_D 47.09. $C_{10}H_{18}O$. Calc. 47.35.

Found %: C 77.90; H 11.82. $C_{10}H_{18}O$. Calculated %: C 77.92; H 11.68.

No hydroxyl groups were detected by the Chugaev-Tserevitinov method.

For the oxidation 11.6 g of the substance of b. p. 79-80° (70 mm), 75 ml of water, and 1 g of potash were used, and with mechanical stirring, 540 ml of a 3% solution of potassium permanganate was added slowly (by consideration of 4 active oxygen atoms). The substance was oxidized at room temperature for 5 days. The distillate with the volatile neutral products, by subsequent saturation with sodium sulfate and removal each time of half the volume, was brought to a 50 ml volume, from which on fractionation by a column with an efficiency of 27 theoretical plates a fraction with a b. p. of 95-97° was removed. A 2,4-dinitrophenylhydrazone which melted at 127-127.5° (from methanol) was formed from this fraction. A test of a mixture with the dinitrophenylhydrazone of acetone produced a depression of the melting point by 27°. No semicarbazone was obtained from this fraction. It was not possible to study the ketone closely because of its small quantity. After the above-indicated fraction was separated, the remaining neutral products were extracted with ether in an extractor for 40-45 hours. From the ether extract 0.7 g of a substance with a b. p. of 105-106° (17 mm), n_D^{20} 1.4630, was isolated, which gave reactions for the keto group with neither semicarbazide nor with 2,4-dinitrophenylhydrazine.

The solution of the salts was acidified with hydrochloric acid, and the volatile acids were steam-distilled.

For the neutralization of the volatile acids, 270.25 ml of 0.093 N NaOH was consumed, which corresponded to 1.0058 g of NaOH.

No traces of formic acid were detected. Acetic acid was determined by the cacodyl test and by an analysis of the silver salt.

Found %: Ag 63.90. $C_2H_3O_2Ag$. Calculated %: Ag 64.07.

From the neutralized solution which remained after the removal of the volatile acids 0.8 g of oxalic acid with a m. p. of 101-102° (test of a mixture) was isolated via calcium oxalate. After removal of the calcium oxalate, the solution was acidified (to methyl violet) with hydrochloric acid and was extracted with ether in an extractor for 30 hours. The extract was dried over sodium sulfate, and after removal of the ether the product was vacuum distilled. It consisted of 1.6 g of a heavy, viscous, bright-green liquid, with a b. p. of 102-103° (2 mm), which gave an acid reaction to litmus. It was poorly soluble in water, but was soluble in alcohol.

Found %: C 58.63, 58.49; H 8.88, 8.70. M 196. $C_{10}H_{18}O_4$. Calculated %: C 59.40; H 8.90. M 202.

The somewhat reduced carbon content, compared with the theoretical, is obviously explained by the inadequate purity of the substance analyzed.

The barium salt was obtained by dissolving a weighed portion of the acid in aqueous alcohol and neutralizing the solution with barium hydroxide (to phenolphthalein). After evaporation of the solvent, the salt was left as a heavy, viscous liquid, which, after treatment with ether, was crystallized.

Found %: Ba 26.58, 26.71. M 189.

3,4,7-Trimethyloctene-5-triol-3,4,7 (II).

3,4,7-Trimethyloctene-5-triol-3,4,7 was prepared by the hydrogenation of 3,4,7-trimethyloctyne-5-triol-3,4,7 [1]. Its b. p. was 117-118° (2 mm), n_D^{20} 1.4774.

Dehydration of 3,4,7-trimethyloctene-5-triol-3,4,7. 30 g of the triol was shaken with 530 ml of 10% sulfuric acid at room temperature until all of the substance was dispersed throughout the total volume as a homogeneous emulsion. In proportion to the shaking, a pleasant odor which later changed to a rather sharp odor appeared, and the mixture gradually acquired a reddish color of a violet shade. The reaction mixture stood for 3 days, after which it was salted out with ammonium sulfate, and the oily layer which formed was separated. Further treatment was carried out just as in the first case. 25.0 g of the crude product was isolated, from which 22.8 g (84%) of a main fraction with a b. p. of 70-72° (8 mm) was distilled, which should be considered 2,2,5,6-tetramethyl-6-ethyldihydropyranol-5 (VI), which was not described in the literature.

With 5% H_2SO_4 the yield amounted to 54%, and with 30% acid it was 56%.

d_4^{20} 0.9442, n_D^{20} 1.4559, MR_D 52.96. $C_{11}H_{20}O_2$ F. Calc. 53.49.

Found %: C 71.59, 71.31; H 10.91, 10.85; OH 9.80. $C_{11}H_{20}O_2$. Calculated %: C 71.74; H 10.87; OH 9.24.

In this case, just as in the preceding, we were unable to obtain any ketone derivative.

Hydrogenation of 2,2,5,6-tetramethyl-6-ethyldihydropyranol-5 (VI). 5.0 g of the substance was hydrogenated over platinum oxide in 50 ml of methanol distilled over alkali hydroxide. The 738 ml of hydrogen calculated for one double bond was absorbed during 245 minutes (20°, 695.3 mm). After this the reaction had practically ceased. After drying with potash the reaction products were vacuum distilled. 3.8 g of 2,2,5,6-tetramethyl-6-ethyltetrahydropyranol (X), which was not described in the literature, was isolated:

B. p. 74.5-75° (8 mm), d_4^{20} 0.9297, n_D^{20} 1.4474, MR_D 53.49. $C_{11}H_{22}O_2$. Calc. 53.96.

Found %: C 70.76; H 11.55; OH 9.34. $C_{11}H_{22}O_2$. Calculated %: C 70.96; H 11.82; OH 9.10.

No derivatives characteristic of the keto group were obtained.

3.4 g of metallic sodium was introduced in small portions into a solution of 4.5 g of the substance in 140 ml of dry methanol, with cooling. After treatment of the reaction products with water, 3.8 g of the unaltered starting material was extracted with ether, which indicated the absence of a keto group.

Dehydration of 2,2,5,6-tetramethyl-6-ethyltetrahydropyranol-5 (X) with potassium bisulfate. 6.0 g of the substance, 3 g of finely-ground anhydrous potassium bisulfate and 0.4 g of pyrogallol were heated on the bath at 147° in vacuo (40 mm). The product which distilled passed into a vessel immersed in a cooling mixture. 5.5 g of a crude product was obtained, which was dried with potash and vacuum distilled. 4 g of 2,2,5,6-tetramethyl-6-ethyl-Δ^4-dihydropyran, which was not described in the literature, was obtained:

B. p. 79-80° (29 mm), d_4^{20} 0.8673, n_D^{20} 1.4466, MR_D 51.71. $C_{11}H_{20}O$ F. Calc. 51.97.

Found %: C 78.12; H 11.95. $C_{11}H_{20}O$. Calculated %: C 78.57; H 11.90.

No hydroxyl groups were detected by the Chugaev-Tserevitinov method.

2.2 g of the substance with a b. p. of 78-80° (29 mm), in 25 ml of water and 0.5 g of potash was oxidized at room temperature with 240 ml of a 3% solution of potassium permanganate (by consideration of 5 active oxygen atoms). The treatment of the reaction products was carried out as in the instances described earlier. From the distillate with the neutral products, a fraction with a b. p. of 70-90° was distilled at ordinary pressure with a fractionating column. A 2,4-dinitrophenylhydrazone which melted at 127-127.5° (from methanol) was isolated from this fraction. We were unable to obtain a semicarbazone from this fraction.

The neutral products, after the above-indicated fraction was separated, were extracted in an extractor for 40 hours. 0.9 g of a substance was isolated:

B. p. 93-100° (8 mm), n_D^{20} 1.4540.

Found %: C 63.28, 63.41; H 10.79, 10.28.

A semicarbazone was obtained, which after recrystallization from ethanol melted at 200-201° (% N 17.17, 16.99). We were unable to obtain a 2,4-dinitrophenylhydrazone from this fraction. The structure of the ketone was not established, because of its small quantity.

For the neutralization of the volatile acids 55 ml of 0.1075 N NaOH was consumed, which corresponded to 0.2365 g of NaOH.

No formic acid was detected in the volatile acids distillate. Acetic acid was detected by the cacodyl test. Its silver salt was obtained.

Found %: Ag 63.30, 63.60. $C_2H_3O_2Ag$. Calculated %: Ag 64.07.

The solution which remained after removal of the volatile acids was neutralized, and 0.1 g of oxalic acid, m. p. 101-102°, was isolated (test of a mixtuqe) from it via calcium oxalate. No other acids were isolated.

2-Methyl-5-(1-hydroxycyclohexyl)-hexene-3-diol-2,5 (III).

2-Methyl-5-(1-hydroxycyclohexyl)-hexene-3-diol-2,5 was prepared by the hydrogenation of 2-methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 [1] and had a m. p. of 102-103°.

Dehydration of 2-methyl-5-(1-hydroxycyclohexyl)-hexene-3-diol-2,5. 15 g of the substance was dehydrated with 360 ml of 10% sulfuric acid under the same conditions as in the first instance. Further treatment was effected in the same way. 11.7 g (84.7%) of a substance, which should be assumed to be 2,2,5-trimethyl-6-spirocyclohexanedihydropyranol-5 (VII), which was not described in the literature, was isolated. With 20 and 30% H_2SO_4 the yield amounted to 63%.

B. p. 108-109° (8 mm), d_4^{20} 0.9984, n_D^{20} 1.4828, MR_D 60.05. $C_{13}H_{22}O_2$F. Calc. 60.53.

Found %: C 74.27, 74.30; H 10.57, 10.59; OH 8.80, 8.50. $C_{13}H_{22}O_2$. Calculated %: C 74.29; H 10.48; OH 8.10.

Reactions for keto group were negative.

Hydrogenation of 2,2,5-trimethyl-6-spirocyclohexanedihydropyranol-5 (VII). 6 g of the substance in 60 ml of methanol was hydrogenated over platinum oxide. During 50 minutes 740 ml of hydrogen was absorbed (15°, 699.9 mm); 730 ml was required for one double bond; after this the reaction had practically ceased. After drying with potash and after vacuum distillation 5.5 g (91.6%) of 2,2,5-trimethyl-6-spirocyclohexanetetrahydropyranol-5 (XI), which was not described in the literature, was isolated:

B. p. 109.5-110° (8 mm), d_4^{20} 0.9848, n_D^{20} 1.4740, MR_D 60.5. $C_{13}H_{24}O_2$. Calc. 61.0

Found %: C 73.77; H 11.30; OH 8.20, 8.04. $C_{13}H_{24}O_2$. Calculated %: C 73.58; H 11.30; OH 8.02.

Reactions for keto group were negative.

Dehydration of 2,2,5-trimethyl-6-spirocyclohexanetetrahydropyranol-5 (XI) with potassium bisulfate. 6.5 g of the substance, 2.5 g of potassium bisulfate and 0.4 g of pyrogallol were heated at about 140° in vacuo at 24 mm. Into a vessel immersed in a cooling mixture, 6.0 g of crude product was distilled, which was dried with potash and distilled at 8 mm. 3 g of the initial product (b. p. 93.5°, n_D^{20} 1.4740) and 3.5 g of 2,2,5-trimethyl-6-spirocyclohexane-Δ^4-dihydropyran, which was not described in the literature, was obtained.

B. p. 108-110° (8 mm), d_4^{20} 0.92706, n_D^{20} 1.4729, MR_D 58.69. $C_{13}H_{22}O$F. Calc. 59.00.

Found %: C 80.20; H 11.23. $C_{13}H_{22}O$. Calculated %: C 80.41; H 11.34.

2,4-Di-(1-hydroxycyclohexyl)-buten-3-ol-2 (IV).

2,4-Di-(1-hydroxycyclohexyl)-buten-3-ol-2 was prepared by the hydrogenation of 2,4-di-(1-hydroxycyclohexyl)-butyn-3-ol-2 [1], and had a m. p. of 111-112°.

Dehydration of 2,4-di-(1-hydroxycyclohexyl)-buten-3-ol-2. 15 g of the substance was dehydrated with 360 ml of 10% sulfuric acid under the same conditions as was the preceding alcohol. The heating of the reaction mixture was continued for approximately 9 hours. As a result, 11.8 g (84.3%) of a pleasant-smelling liquid which should be considered 5-methyl-2,6-dispirocyclohexanedihydropyranol-5 (VIII), which was not described in the literature, was isolated. With 20% H_2SO_4 the yield was 79%.

B. p. 121-122° (12 mm), d_4^{20} 1.0365, n_D^{20} 1.5055, MR_D 71.66. $C_{16}H_{22}O_2$ F. Calc. 72.18.

Found %: C 76.97, 76.91; H 10.69, 10.41; OH 6.99, 6.91. $C_{16}H_{26}O_2$. Calculated %: C 76.80; H 10.40; OH 6.80.

Reaction for keto group was negative.

Hydrogenation of 5-methyl-2,6-dispirocyclohexanedihydropyranol-5 (VIII). 9 g of the substance in 90 ml of methanol was hydrogenated over platinum oxide. The hydrogenation proceeded very slowly for several days. On the average the temperature was 17° and the pressure was 688 mm. A total of 925 ml of hydrogen was absorbed; the calculated quantity of hydrogen for saturation was 950 ml. From the reaction products after drying with potash, 8.2 g (91 1%) of 5-methyl-2,6-dispirocyclohexanetetrahydropyranol-5, which was not described in the literature, was distilled.

B. p. 118-119° (2 mm), d_4^{20} 1.0227, n_D^{20} 1.4963, MR_D 72.04. $C_{16}H_{28}O_2$. Calc. 72.65.

Found %: C 76.37; H 11.03; OH 6.08, 6.70. $C_{16}H_{28}O_2$. Calculated %: C 76.19; H 11.11; OH 6.74.

Reactions for keto group were negative.

SUMMARY

1. On treatment with sulfuric acid, the tertiary ethylenic glycerols dehydrated, liberating one molecule of water, with the formation of unsaturated alcohols of the heterocyclic series.

2. Most likely the heterocycles which formed should belong to the substituted dihydropyranols.

3. Over a platinum catalyst, all the resulting substituted dihydropyranols hydrogenated to the corresponding tetrahydropyranols, absorbing one molecule of hydrogen.

4. Upon vacuum distillation in the presence of potassium bisulfate the substituted tetrahydropyranols readily dehydrated to the corresponding dihydropyrans.

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SYNTHETIC ANESTHETIC SUBSTANCES

I. ESTERS OF 1-ALKYL-1-PHENYL-3-DIALKYLAMINOPROPANOLS-1

I. N. Nazarov and E. M. Cherkasova

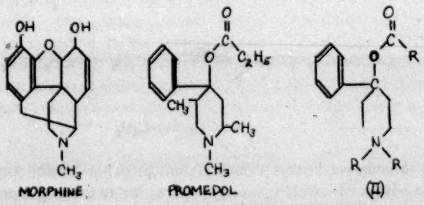
In the field of synthetic medicinal substances, investigations of the last few decades have shown conclusively that the complete synthesis of natural physiologically active complex compounds is not always brought about expediently, and that in a number of instances the synthetic preparations which are simpler in structure considerably surpass the natural compounds in activity.

After the obtaining of novocaine [1] (ester of p-aminobenzoic acid and β-diethylaminoethanol) a vast number of other anesthetics were synthesized, the structure of which reproduced the basic elements of the so-called "anesthetiphoric" group $>N-(C)_n-OCOAr$, in one form or another. The majority of these compounds belong to the class of the esters of aromatic acids and dialkylaminoalkanes, i. e., are analogs and homologs of novocaine.

However, in spite of the abundance of works in this field, up to the present time intensified searches for local anesthetics have not ceased. This indicates that the known preparations do not satisfy all of the requirements of contemporary surgery. The anesthetics most applicable at the present time (dicaine, etc.), although somewhat more powerful than novocaine, are much more toxic than it is. Thus, it is impossible to consider the problem of the synthesis of local anesthetics as completely solved, and further investigations in this field continue to remain essential.

In connection with this, the problem of carrying out a systematic synthesis of various esters of aliphatic-aromatic amino alcohols of the $>N-(C)_n-\underset{\displaystyle Ar}{\overset{|}{C}}-OCOR$ type was posed for the purpose of the investigation of new highly-active medicinal substances (chiefly anesthetics) and the establishment of a relationship between the structure of these compounds and their physiological activity.

The esters of 1-alkyl-1-phenyl-3-dialkylaminopropan-1 -ols (II) may be considered as "cuts" in the piperidine cycle of the esters of 4-phenyl-4-piperidols, among which were recently found the most powerful anesthetic substances, which surpass the activity of morphine by several times (promedol, et al.) [2, 3].

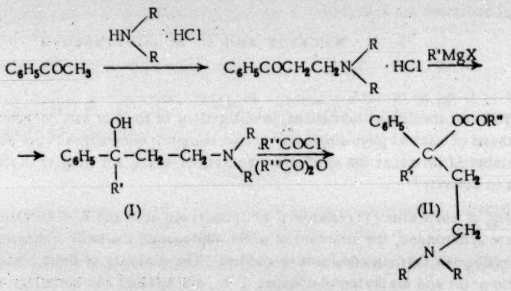


When the present investigation, begun in 1948, was to a large extent completed, several works were published, which were devoted to the amino ketones, and the alkylarylaminoalkanols [4] and their dehydration products [4-8], but the esters of aliphatic-aromatic amino alcohols have been studied very little [6-8].

For the realization of the projected program, we first synthesized a systematic series of esters of 1-alkyl-1-phenyl-3-dialkylaminopropanols-1 (II) with a normal (unbranched) propanol chain. The latter was obtained as a result of the reaction of Grignard reagents with β-dialkylaminopropiophenones, which were synthesized from

acetophenone secondary amines and formaldehyde by the Mannich reaction [9]. The majority of the amino alcohols (I) were obtained in high yields (80-90%) by the action of Grignard reagents (3-fold excess) on amino ketone hydrochlorides, whereas the Grignard reagent with the same amino ketones usually leads to the production of amino alcohols in very low yields (10-20%) [4]. The resulting amino alcohols were esterified by means of the hydrochlorides (sometimes anhydrides) of the corresponding acids, usually in the presence of magnesium [10].

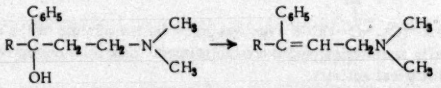
By such a method, under mild conditions, we were able to obtain in high yields (70-90%) almost all of the esters planned:



$R = CH_3, C_2H_5$; $R' = CH_3, C_2H_5, C_3H_7, C_4H_9$ et al.;
$R'' = CH_3, C_2H_5, C_6H_5OCH_2, C_6H_5, C_6H_5CH{=}CH, C_6H_5CH_2CH_2$.

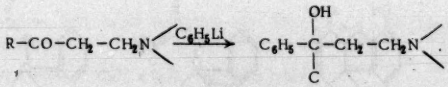
Only for 1-ethyl-1-phenyl-3-diethylaminopropanol-1 were we unable to obtain the esters by any of the methods tested.

In some instances esterification was accompanied by dehydration of the alcohols:



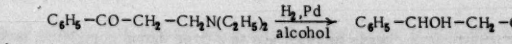
$R = C_2H_5$, iso-C_4H_9

Some tertiary 1-alkyl-1-phenyl-3-dialkylaminopropanols-1 were obtained in a 40-60% yield by the action of phenyllithium on the appropriate aliphatic amino ketones:



$R = CH_3$, iso-C_4H_9

The phenoxyacetate of secondary 1-phenyl-3-diethylaminopropanol-1 also, obtained by the hydrogenation of β-diethylaminopropiophenone with a Pd-catalyst, was synthesized for an investigation of physiological activity.



It should be noted that the hydrogenation of the hydrochloride of this amino ketone in an aqueous solution leads to its cleavage to diethylamine and propiophenone.

The esters described in this paper were isolated directly as the hydrochlorides, which were stable, crystalline, colorless substances, which dissolved readily in water. The free amino alcohols and their esters were liquids or low-melting crystalline compounds with a specific amine odor, and they gradually turned yellow on storage. Some of the

compounds which we synthesized, as the hydrochlorides, were subjected to a pharmacological investigation and showed an interesting physiological activity.* The most interesting compound proved to be the phenoxyacetate of 1-ethyl-1-phenyl-3-dimethylaminopropanol-1, which had a very powerful anesthetizing activity equal to that of dicaine but 4-5 times less toxic than the latter. Moreover, this preparation had a spasmolytic activity and brought about a considerable lowering of the blood pressure.

None of the esters tested (among them the propionates) had a sedative effect and, consequently, the opening of the piperidine ring in promedol and compounds similar to it led to a complete loss of anesthetic activity. A similar observation was also made recently by other authors [7].

EXPERIMENTAL **

1-Phenyl-3-diethylaminopropanol-1 (I, R'=H, R = C_2H_5)

a) 5 g of β-diethylaminopropiophenone hydrochloride (m. p. 106-107°) in 60 ml of anhydrous ethyl alcohol was hydrogenated in the presence of palladium on calcium carbonate (5% Pd). The hydrogenation was continued for 7 hours; after this time 0.45 g of the catalyst was introduced in small portions (about 0.1 g). 224 ml of hydrogen, as compared to 214 ml calculated theoretically, was absorbed. The catalyst was filtered off, the alcohol was removed, the residue was dissolved in water and acidified with 20% hydrochloric acid, and the neutral products were extracted with ether. The acidic aqueous solution was saturated with soda and extracted with ether (150 ml), the ether solution was dried with sodium sulfate, and after removal of the ether the residue was vacuum distilled. 2 g (46.6%) of 1-phenyl-3-diethylaminopropanol-1 was obtained.

B. p. 113-113.5° (2 mm).

Found %: C 74.91, 75.04; H 10.32, 10.00; N 6.80, 6.90. $C_{13}H_{21}ON$. Calculated %: C 75.20; H 10.13; N 6.75

b) 5 g of β-diethylaminopropiophenone hydrochloride in 75 ml of water was hydrogenated in the presence of a Pd-catalyst (a total of 0.31 g). The absorption of hydrogen took place much more rapidly than on hydrogenation in an alcoholic solution.

500 ml of hydrogen was absorbed. A crystalline substance and an oil remained after removal of the water. After crystallization from alcohol and acetone, the crystals melted at 224° and gave no depression with the pure diethylamine hydrochloride (m. p. 225°). The oil was extracted with ether (200 ml), dried with sodium sulfate and vacuum distilled. 2.4 g (81%) of propiophenone with a b. p. of 89-91° (9 mm) was obtained. The semicarbazone melted at 172-173° and gave no depression with the known form.

1-Ethyl-1-phenyl-3-diethylaminopropanol-1 (I, R' = R = C_2H_5)

An ether solution of ethylmagnesium bromide was prepared from 4.5 g of magnesium, 20.4 g of ethyl bromide and 65 ml of anhydrous ether.

13 g of β-diethylaminopropiophenone hydrochloride (m. p. of 108°) was added gradually to this solution at a temperature of −10°, with stirring. The mixture was left overnight, and on the next day the product was made acid to Congo with dilute hydrochloric acid (1:1), the ether layer was separated, and the aqueous layer was saturated with solid alkali and extracted with ether. Dry hydrogen chloride was passed through an ether solution of the amino alcohol and the hydrochloride precipitate which formed was recrystallized from a mixture of anhydrous alcohol and ether. 6.9 g (47.3%) of 1-ethyl-1-phenyl-3-diethylaminopropanol-1 hydrochloride with a m. p. of 162-163° was obtained [4].

Found %: N 5.01, 5.20. $C_{15}H_{26}ONCl$. Calculated %: N 5.16.

4-Dimethylaminobutanone-2. 40 ml of 33% dimethylamine was added to 22 g of 4-methoxybutanone-2 (b. p. 140-141° at 750 mm) [12, 13]. The solution was heated on the water bath at 80° for 5 hours. On the next day the solution was acidified with hydrochloric acid and was extracted twice with ether, but no neutral products were found. The acidified aqueous layer was saturated with potash, extracted several times with ether, the ether extract was dried with sodium sulfate, the ether was removed and the product was vacuum distilled. 20 g (80%) of 4-dimethylaminobutanone-2, of b. p. 50-52° (13 mm), was obtained [13].

* The tests were made by M. D. Mashkovsky in the S. Ordzhonikidze All Union Sci. Res. Inst. Pharm. Chem.

** I. Nikolaeva, M. Kogan, A. Kosmovskaya and Yu. Segal participated in the experimental work.

1-Methyl-1-phenyl-3-dimethylaminopropanol-1 (I, R' = R = CH_3)

1.3 g of lithium and 40 ml of anhydrous ether were charged into a three-necked flask, equipped with a thermometer, dropping funnel, reflux condenser, stirrer and tube for the passage of nitrogen, and 14.4 g of bromobenzene in 40 ml of ether was added gradually. On the next day at a temperature of −10-14°, 9 g of 4-dimethylaminobutanone-2 in 30 ml of ether was added dropwise. The mixture was left overnight, and on the next day was stirred for 3 hours more at the boiling point of ether. The product was treated with dilute hydrochloric acid, the ether layer was separated, the aqueous layer was extracted once more with ether for complete removal of the bromobenzene and biphenyl, saturated with potash and again repeatedly extracted with ether. The ether extracts were dried with sodium sulfate, and the product was vacuum distilled.

5.2 g of 1-methyl-1-phenyl-3 dimethylaminopropanol-1 was obtained as a colorless liquid with a b. p. of 102-103° (4.5 mm). The hydrochloride melted at 160-161° [6].

1-Ethyl-1-phenyl-3-dimethylaminopropanol-1 (I, R' = C_2H_5, R = CH_3)

12 g of β-dimethylaminopropiophenone (m. p. 153°) was added gradually [9], with vigorous stirring, to a solution of ethylmagnesium bromide, prepared from 4 g of magnesium and 18.3 g of ethyl bromide in 80 ml of anhydrous ether, at a temperature of −8-12°. Stirring was continued for 1 hour at room temperature after the addition of the amino ketone; the reaction mixture was left overnight, and on the next day was stirred 2 hours more at the boiling point of the ether. The product was treated with dilute hydrochloric acid (1:1), with cooling and stirring, until there was an acid reaction to Congo, the ether layer was separated, and the aqueous layer was saturated with solid sodium hydroxide and repeatedly extracted with ether. The ether extracts were dried with sodium sulfate, the ether was removed, and the product was vacuum distilled. 10 g (85%) of 1-ethyl-1-phenyl-3-dimethylaminopropanol-1 with a b. p. of 90-92° (1 mm) was obtained, which, after some time, crystallized and melted at 42-43° [4].

Found %: N 7.00, 6.77. $C_{13}H_{21}ON$. Calculated %: N 6.75.

1-n-Propyl-1-phenyl-3-dimethylaminopropanol-1 (I, R' = n-C_3H_7, R = CH_3)

A solution of propylmagnesium bromide, prepared from 14.4 g of magnesium, 73.8 g of freshly-distilled propyl bromide (b. p. 70-71°) and 200 ml of anhydrous ether, was put into a three-necked round-bottomed flask, equipped with a mechanical stirrer with a mercury seal, a reflux condenser and thermometer. 42.7 g of β-dimethylaminopropiophenone hydrochloride was added gradually to this solution at a temperature of −8-12°, with vigorous stirring. Stirring was continued for 2 hours; after the addition of the ketone, the reaction substance was left overnight, and on the next day was again stirred at the boiling point of ether for 3 hours. The product was hydrolyzed by the addition of 100 g of ice, 150 ml of 25% ammonium chloride and 100 ml of acetic acid. * The ether layer was separated, and the aqueous layer was extracted 2 times with ether in order to remove the neutral products. Then the aqueous layer was treated with 25% ammonia (potash or solid alkali could be used) and was repeatedly extracted with ether. The ether extracts were dried with sodium sulfate, the ether was removed, and the product was vacuum distilled. 32.4 g (73%) of 1-n-propyl-1-phenyl-3-diethylaminopropanol-1 with a b. p. of 102-104° (1 mm) was obtained, which, after recrystallization from a mixture of alcohol and acetone, melted at 49-50°.

Found %: N 6.50, 6.29. $C_{14}H_{23}ON$. Calculated %: N 6.32.

The amino alcohol hydrochloride after 2 recrystallizations from alcohol melted at 151-152°.

Found %: N 5.51, 5.47. $C_{14}H_{24}ONCl$. Calculated %: N 5.44.

1-Isopropyl-1-phenyl-3-dimethylaminopropanol-1 (I, R' = iso-C_3H_7, R = CH_3)

6 g of β-dimethylaminopropiophenone hydrochloride was added gradually to a solution of isopropylmagnesium bromide, prepared from 2.7 g of magnesium and 14.8 g of freshly-distilled isopropyl bromide (b. p. 59-60°) in 50 ml of anhydrous ether, with vigorous stirring and with cooling to −10-12°.

The mixture was stirred at room temperature for 2 hours, left overnight and on the next day was again stirred for 2 hours at the boiling point of ether. After hydrolysis with dilute hydrochloric acid (1:1), saturation of the aqueous layer with solid alkali, careful extraction with ether and distillation, 3.1 g (55.5%) of 1-isopropyl-1-phenyl-3-dimethylaminopropanol-1 was obtained.

B. p. 96-97° (1 mm), n_D^{20} 1.5222, d_4^{20} 0.9893, MR_D 68.25; calc. 68.71.

Found %: N 6.51, 6.53. $C_{14}H_{23}ON$. Calculated %: N 6.32.

* As in the preceding experiment, it can also be hydrolyzed with hydrochloric acid.

The hydrochloride melted at 152-153° (from alcohol).

Found %: N 5.62, 5.56. $C_{14}H_{24}ONCl$. Calculated %: N 5.44.

1-n-Butyl-1-phenyl-3-dimethylaminopropanol-1 (I, R' = n-C_4H_9, R = CH_3)

5.4 g of magnesium, 31 g of n-butyl bromide (b. p. 100-101°), 12 g of β-dimethylaminopropiophenone hydrochloride and 60 ml of anhydrous ether were used in the reaction. The reaction was carried out as described in the preceding experiments, and 10 g (80%) of 1-n-butyl-1-phenyl-3-dimethylaminopropanol-1 with a m. p. of 43-44° was obtained [6].

Found %: N 5.98, 5.87. $C_{15}H_{25}ON$. Calculated %: N 5.95.

The hydrochloride melted at 148-150° (from alcohol).

Found %: N 5.20, 5.41. $C_{15}H_{26}ONCl$. Calculated %: N 5.16.

1-Isobutyl-1-phenyl-3-dimethylaminopropanol-1 (I, R' = iso-C_4H_9, R = CH_3)

4.9 g of metallic lithium and 40 ml of anhydrous ether were charged into a three-necked flask equipped with a thermometer, dropping funnel, reflux condenser with calcium chloride tube, stirrer and tube for passage of nitrogen, and a solution of 75 g of bromobenzene in 50 ml of anhydrous ether was added dropwise. The reaction was carried out in an atmosphere of dry nitrogen. After the formation of phenyllithium, with good cooling (ice and salt), a solution of 50 g of 2-methyl-6-dimethylaminohexanone-4 (b. p. 72-74° at 8 mm) in 70 ml of anhydrous ether was added dropwise [14]. The mixture was left overnight, and on the next day it was heated at the boiling point of ether for 3 hours. After cooling, we hydrolyzed the reaction substance with hydrochloric acid (1:1), the ether layer was separated, and the aqueous layer was extracted once more with ether. After this the aqueous layer was saturated with solid potassium hydroxide, with cooling with ice, and the product was repeatedly extracted with ether and dried with sodium sulfate. After removal of the ether, the residue crystallized and was recrystallized from gasoline. 40 g of 1-isobutyl-1-phenyl-3-dimethylaminopropanol-1 was obtained.

M. p. 64-65°, b. p. 115-116° (1.5 mm).

Found %: N 5.99, 5.72. $C_{15}H_{25}ON$. Calculated %: N 5.95.

The hydrochloride melted at 142-142.5°, the iodomethylate at 217-217.5°, and the oxalate at 155-156°.

1-Benzyl-1-phenyl-3-dimethylaminopropanol-1 (I, R' = $C_6H_5CH_2$, R = CH_3)

The reaction was carried out as described above for 1-n-propyl-1-phenyl-3-dimethylaminopropanol-1. 53 g (70%) of 1-benzyl-1-phenyl-3-dimethylaminopropanol-1 with a m. p. of 70-72° was obtained [8, 15] from 60 g of β-dimethylaminopropiophenone hydrochloride, 95.5 g of benzyl chloride and 18.3 g of magnesium.

Found %: N 5.07. $C_{18}H_{23}ON$. Calculated %: N 5.20.

The hydrochloride melted at 156-157°.

Found %: N 4.18, 4.28. $C_{18}H_{24}ONCl$. Calculated %: N 4.58.

The acid chloride of phenoxyacetic acid. A mixture of 269 g of thionyl chloride and 63.3 g of phenoxyacetic acid (m. p. 97-98°, obtained from phenol and chloroacetic acid) was heated at 80° for 6 hours. On the next day, the excess of thionyl chloride was removed, and the residue was vacuum distilled. 58.3 g (82%) of the acid chloride of phenoxyacetic acid with a b. p. of 109-110° (11 mm) was obtained [16].

Phenoxyacetate of 1-phenyl-3-diethylaminopropanol-1 (II, R' = H, R'' = $CH_2OC_6H_5$, R = C_2H_5)

9.27 g of the acid chloride of phenoxyacetic acid in 6 ml of toluene was added gradually to 4.5 g of 1-phenyl-3-diethylaminopropanol-1 in 6 ml of toluene. Dry hydrogen chloride was passed through the resulting solution for 10-15 minutes, and then the mixture was heated on the water bath for 1.5 hours. On the next day, the reaction substance was acidified with hydrochloric acid (1:1), the neutral products were extracted with ether, the aqueous layer was treated with soda, and the basic products were repeatedly extracted with ether, dried with sodium sulfate and vacuum distilled. 5.43 g (98%) of the phenoxyacetate of 1-phenyl-3-diethylaminopropanol-1 with a b. p. of 171-172° (1 mm) and 1.2 g of the original alcohol were obtained.

Found %: C 73.90, 73.62; H 8.27, 8.25; N 4.27, 4.42. $C_{21}H_{27}O_3N$. Calculated %: C 73.90; N 7.92; N 4.11.

The oxalate of the phenoxyacetate melted at 103-105°.

Found %: C 63.62, 63.71; H 6.44, 6.63; N 3.46, 3.62. $C_{23}H_{29}O_7N$. Calculated %: C 63.95; H 6.72; N 3.24.

The Acetate of 1-Methyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = R'' = R = CH_3)

a) 6 g of 1-methyl-1-phenyl-3-dimethylaminopropanol-1, 0.42 g of magnesium, and 30 ml of anhydrous benzene were placed in a round-bottomed flask equipped with a reflux condenser with a calcium chloride tube, and 7 g of freshly-distilled acetyl chloride was added gradually. An evolution of heat was observed, and before long the colorless precipitate of the acetate hydrochloride came down. For completion of the reaction the mixture was heated for 20 minutes at 85-90°, after which the benzene was removed and a solution of soda was added to the cooled residue. The oil which came to the surface was extracted with ether, dried with sodium sulfate and vacuum distilled. 6.4 g of the acetate of 1-methyl-1-phenyl-3-dimethylaminopropanol-1 was obtained as a viscous, slightly yellow liquid with a b. p. of 94-96° (1.5 mm).

Found %: N 6.11, 6.17. $C_{14}H_{21}O_2N$. Calculated %: N 5.95.

b) 2 g of 1-methyl-1-phenyl-3-dimethylaminopropanol-1, 2.4 g of acetyl chloride and 15 ml of anhydrous benzene were used. After 5 minutes, the reaction mixture had crystallized. After 2 recrystallizations from a mixture of acetone and chloroform 2.4 g of the acetate hydrochloride of 1-methyl-1-phenyl-3-dimethylaminopropanol-1 with a m. p. of 175.5-176° was obtained [6].

Found %: N 4.80. $C_{14}H_{22}O_2NCl$. Calculated %: N 5.15.

Propionate of 1-Methyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = R = CH_3, R'' = C_2H_5)

6 g of 1-methyl-1-phenyl-3-dimethylaminopropanol-1, 0.42 g of magnesium, and 30 ml of anhydrous benzene were introduced into a round-bottomed flask with a reflux condenser and a calcium chloride tube, and 6.4 g of propionyl chloride was added gradually. A strong evolution of heat was observed, and before long the colorless precipitate of the propionate hydrochloride came down. After the evolution of heat ceased, the mixture was heated at 85-90° for 2 hours. After the treatments described in the preceding experiment, 5.8 g of the propionate of 1-methyl-1-phenyl-3-dimethylaminopropanol-1 with a b. p. of 97-99° (1.5 mm) was isolated.

Found %: N 5.35, 5.66. $C_{15}H_{23}O_2N$. Calculated %: N 5.61.

The hydrochloride of the ester was readily obtained in a high yield (2.3 g of the ester hydrochloride was isolated from 2 g of the amino alcohol) directly by the esterification reaction, and after recrystallization from acetone melted at 154.5-155°.

Found %: N 4.78. $C_{15}H_{24}O_2NCl$. Calculated %: N 4.90.

Benzoate of 1-Methyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = R = CH_3, R'' = C_6H_5)

6 g of 1-methyl-1-phenyl-3-dimethylaminopropanol-1, 0.42 g of magnesium, and 30 ml of anhydrous benzene were charged into a round-bottomed flask with a reflux condenser and a calcium chloride tube, and 9.73 g of benzoyl chloride was introduced gradually. An evolution of heat was observed, and before long a colorless precipitate came down. For completion of the reaction, the mixture was heated at 100° for 2 hours. After the treatment described in the preceding experiment, 7.1 g of the benzoate of 1-methyl-1-phenyl-3-dimethylaminopropanol-1, with a b. p. of 156-158° (2 mm), was isolated as a yellow, viscous liquid.

Found %: N 4.62, 4.69. $C_{19}H_{23}O_2N$. Calculated %: N 4.71.

The hydrochloride of the benzoate could readily be formed directly by the esterification reaction. On mixture of 2 g of amino alcohol, 3.2 g of benzoyl chloride and 15 ml of anhydrous benzene, 2.6 g of the benzoate hydrochloride with a m. p. of 180-180.5° (from acetone) was obtained [6].

Found %: N 4.20. $C_{19}H_{24}O_2NCl$. Calculated %: N 3.90.

Acetate of 1-Ethyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = C_2H_5, R'' = R = CH_3)

0.15 g of magnesium and 2.64 g of acetyl chloride were added to a solution of 3.2 g of 1-ethyl-1-phenyl-3-dimethylaminopropanol-1 in 30 ml of anhydrous benzene. The reaction proceeded with an evolution of heat, and before long all of the substance had crystallized. The mixture was heated for 10 minutes at 50-60°, after which the excess of acetyl chloride and benzene were vacuum distilled. The residue was washed 2 times with dry ether, dissolved in 15 ml of water, treated with soda, and the product was extracted three times with portions of ether, dried

with sodium sulfate and vacuum distilled.

2.25 g (85%) of the acetate of 1-ethyl-1-phenyl-3-dimethylaminopropanol-1 with a b. p. of 115-117° (1 mm) was obtained.

Found %: N 5.55, 5.86. $C_{15}H_{23}O_2N$. Calculated %: N 5.63.

The hydrochloride after reprecipitation from anhydrous alcohol with dry ether melted at 172-173° [7].

Found %: N 5.02, 5.01. $C_{15}H_{24}O_2NCl$. Calculated %: N 4.83.

Propionate of 1-Ethyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = R'' = C_2H_5, R = CH_3)

4.14 g of the amino alcohol, 20 ml of anhydrous benzene, 0.3 g of magnesium and 4.26 g of propionyl chloride were mixed. The reaction was accompanied by an evolution of heat and after 20-30 minutes the crystallizing precipitate of the propionate hydrochloride formed. The mixture was heated at 70-80° and was treated as described in the preceding experiment. 3.8 g (72%) of the propionate of 1-ethyl-1-phenyl-3-dimethylaminopropanol-1 with a b. p. of 120-122° (2 mm) was obtained.

Found %: N 5.38, 5.23. $C_{16}H_{25}O_2N$. Calculated %: N 5.30.

The hydrochloride after reprecipitation with dry ether from anhydrous alcohol melted at 153-153.5° [7].

Found %: N 4.85, 4.73. $C_{16}H_{26}O_2NCl$. Calculated %: N 4.66.

Benzoate of 1-Ethyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = C_2H_5, R'' = C_6H_5, R = CH_3)

3 g of the amino alcohol, 0.15 g of magnesium, 15 ml of anhydrous benzene and 3.68 g of benzoyl chloride were used in the reaction. A small evolution of heat was observed, but no crystalline precipitate formed. The mixture was heated at 60-80° for 2 hours. As a result of the treatment described in the preceding experiments, 3.2 g (74%) of the benzoate of 1-ethyl-1-phenyl-3-dimethylaminopropanol-1 was obtained as a pale-yellow, viscous liquid with a b. p. of 139-142° (1 mm).

Found %: N 4.58, 4.72. $C_{20}H_{25}O_2N$. Calculated %: N 4.50.

The hydrochloride after reprecipitation from anhydrous alcohol with anhydrous ether melted at 131-131.5°.

Found %: N 4.24, 4.29. $C_{20}H_{26}O_2NCl$. Calculated %: N 4.02.

Phenoxyacetate of 1-Ethyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = C_2H_5, R'' = $CH_2OC_6H_5$, R = CH_3)

2 g of magnesium was added to a solution of 17.5 g of the amino alcohol in 90 ml of anhydrous ether and, with cooling, 21.6 g of freshly-distilled phenoxyacetic acid hydrochloride was added dropwise. After standing for a day, all of the substance had crystallized. The precipitate was washed several times (6-8) with ether, after which the resulting phenoxyacetate hydrochloride melted at 123-129°. Its weight was 37 g. After 2 recrystallizations from dry acetone 20 g (63%) of the colorless phenoxyacetate hydrochloride of 1-ethyl-1-phenyl-3-dimethylaminopropanol-1 with a m. p. of 132-133° was obtained.

Found %: C 67.00, 66.75; H 7.72, 7.70; N 3.64, 4.19; Cl 9.30, 9.42. $C_{21}H_{28}O_3NCl$. Calculated %: C 66.80; H 7.46; N 3.71; Cl 9.42.

The solvent was removed from the mother liquor, and the residue was treated with soda. After vacuum distillation of the dehydration product, the 1-ethyl-1-phenyl-3-dimethylaminopropanol-1 described below with a b. p. of 87-89° (2.5 mm) was obtained.

Found %: N 6.89, 6.91. $C_{13}H_{19}N$. Calculated %: N 7.41.

The hydrochloride melted at 183-184° (from acetone).

Dehydration of 1-Ethyl-1-phenyl-3-dimethylaminopropanol-1. A mixture of 10.4 g of the amino alcohol, 24 g of thionyl chloride and 15 ml of benzene was heated for half an hour at 80°. Then at low vacuum the solvent was removed, and the residue was treated with soda. The product was extracted with ether, dried with sodium sulfate and vacuum distilled. 2.5 g of 5-dimethylamino-3-phenyl-3-pentene $C_6H_5-C(C_2H_5)=CH-CH_2N(CH_3)_2$ with a b. p. of 86-88° (2 mm) was obtained.

Found %: N 7.42, 7.17. $C_{13}H_{19}N$. Calculated %: N 7.41.

The hydrochloride melted at 183-183.5° (from a mixture of acetone and alcohol) and gave no depression with the hydrochloride obtained in the preceding experiment.

Found %: N 6.00, 5.80. $C_{13}H_{20}NCl$. Calculated %: N 6.20.

The Cinnamate of 1-Ethyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = C_2H_5, R'' = CH=CH−C_6H_5, R = CH_3.

0.5 g of magnesium was added to a solution of 6.21 g of the amino alcohol in 8 ml of anhydrous benzene, and 8 g of the acid chloride of cinnamic acid (b. p. 105-107° at 5 mm) [17] in 7 ml of anhydrous benzene was added. On the next day the precipitate which came down was filtered off, washed repeatedly with anhydrous ether and recrystallized 3 times from anhydrous acetone. 2.8 g of the cinnamate hydrochloride of 1-ethyl-1-phenyl-3-dimethylaminopropanol-1 with a m. p. of 163-164° was obtained. In addition 1 g of a substance with the same melting point (after several recrystallizations from acetone) formed from the mother liquor. Its yield was 34%.

Found %: C 70.50, 70.75; H 7.94, 8.01; N 3.60, 3.72. $C_{22}H_{28}O_2NCl$. Calculated %: C 70.70; H 7.50; N 3.75.

The Hydrocinnamate of 1-Ethyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = C_2H_5, R'' = $CH_2CH_2C_6H_5$, R = CH_3)

0.17 g of magnesium was added to a solution of 1.7 g of the amino alcohol in 5 ml of anhydrous benzene, and with cooling, 2.08 g of the acid chloride of hydrocinnamic acid (b. p. 102-103° at 10 mm), obtained in a 93% yield from hydrocinnamic acid and thionyl chloride, was added. On the next day the precipitate which came down was washed with anhydrous ether and was recrystallized several times from anhydrous acetone. 1.8 g (58%) of the hydrocinnamate hydrochloride of 1-ethyl-1-phenyl-3-dimethylaminopropanol-1 with a m. p. of 168-169° was obtained.

Found %: C 69.90; H 7.94; N 3.97, 3.81. $C_{22}H_{30}O_2NCl$. Calculated %: C 70.30; H 7.98; N 3.72.

The Acetate of 1-n-Propyl-1-phenyl-3-dimethylaminopropanol-1(II, R' = n-C_3H_7, R'' = R = CH_3)

0.1 g of magnesium was added to a solution of 2 g of 1-n-propyl-1-phenyl-3-dimethylaminopropanol-1 (m. p. 49-50°) in 10 ml of anhydrous benzene, and 4.3 g of acetyl chloride was added gradually. An evolution of heat was observed, and before long all of the substance had crystallized. On the next day the benzene and the excess acetyl chloride were removed at low vacuum. We washed the remaining crystalline substance with ether, dissolved it in water and saturated it with dry soda. The oil which formed was extracted with ether (4 times at the rate of 20 ml), the ether extract was dried with calcined sodium sulfate, the ether was removed, and the residue was vacuum distilled. 1.4 g (59%) of the acetate of 1-n-propyl-1-phenyl-3-dimethylaminopropanol-1 was obtained.

B. p. 114-115° (1 mm), n_D^{20} 1.4988, d_4^{20} 0.9883, MR_D 78.23; calc. 78.08.

Found %: N 5.61, 5.68. $C_{16}H_{25}O_2N$. Calculated %: N 5.32.

The hydrochloride melted at 164-165.5°(from alcohol).

Found %: N 4.41, 4.70. $C_{16}H_{26}O_2NCl$. Calculated %: N 4.67.

The Propionate of 1-n-Propyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = n-C_3H_7, R'' = C_2H_5, R = CH_3)

0.13 g of magnesium and 2.31 g of freshly-distilled propionyl chloride were added to a solution of 3 g 1-n-propyl-1-phenyl-3-dimethylaminopropanol-1 in 14 ml of anhydrous benzene. An evolution of heat was observed, and before long all of the substance had crystallized. On the next day the reaction substance was heated on the water bath for half an hour and treated as described in the preceding experiment. 2.52 g of the propionate of 1-n-propyl-1-phenyl-3-dimethylaminopropanol-1 was obtained.

B. p. 120-121° (1 mm), n_D^{20} 1.4952, d_4^{20} 0.9804, MR_D 82.54; calc. 82.69.

Found %: N 5.29, 5.31. $C_{17}H_{27}O_2N$. Calculated %: N 5.05.

The hydrochloride melted at 152-153° (from alcohol).

Found %: N 4.31, 4.78. $C_{17}H_{28}O_2NCl$. Calculated %: N 4.46.

The Benzoate of 1-n-Propyl-1-phenyl-3-dimethylaminopropanol-1 (II, $R' = n\text{-}C_3H_7$, $R'' = C_6H_5$, $R = CH_3$)

0.29 g of magnesium was added to a solution of 6.63 g of the amino alcohol in 15 ml of anhydrous benzene, and 9.15 g of benzoyl chloride was added gradually. On the next day the mixture was heated for 2.5 hours at the boiling point of benzene, and was treated as usual. 2 g of the benzoate of 1-n-propyl-1-phenyl-3-dimethylaminopropanol-1 with a b. p. of 158-160° (1 mm) was obtained.

Found %: N 4.37, 4.40. $C_{21}H_{27}O_2N$. Calculated %: N 4.30.

The hydrochloride melted at 112-114° (from alcohol).

Found %: N 3.56, 3.88. $C_{21}H_{28}O_2NCl$. Calculated %: N 3.88.

The picrate melted at 157-158° (from alcohol).

Found %: N 10.23, 10.15. $C_{27}H_{30}O_9N_4$. Calculated %: N 10.10.

The Acetate of 1-Isopropyl-1-phenyl-3-dimethylaminopropanol-1 (II, $R' = iso\text{-}C_3H_7$, $R'' = R = CH_3$)

0.19 g of magnesium was added to a solution of 4.43 g of 1-isopropyl-1-phenyl-3-dimethylaminopropanol-1 (b. p. 96-97° at 1 mm) in 10 ml of anhydrous benzene, and 3.4 g of acetyl chloride was added gradually. The reaction substance was warmed up and before long almost all of it had crystallized. On the next day, the mixture was heated at 80° for 1 hour and was treated as usual. 1.11 g of the acetate of 1-isopropyl-1-phenyl-3-dimethylaminopropanol-1 was obtained.

B. p. 101-102° (0.5 mm), n_D^{20} 1.5058, d_4^{20} 0.9997, MR_D 78.27; calc. 78.08.

Found %: N 5.60, 5.64. $C_{16}H_{25}O_2N$. Calculated %: N 5.32.

The hydrochloride melted at 182-182.5° (from acetone) and was obtained directly from the reaction substance in a yield of 70%.

Found %: N 4.51, 4.54. $C_{16}H_{26}O_2NCl$. Calculated %: N 4.67.

The Propionate of 1-Isopropyl-1-phenyl-3-dimethylaminopropanol-1 (II, $R' = iso\text{-}C_3H_7$, $R'' = C_2H_5$, $R = CH_3$)

To a solution of 1.4 g of amino alcohol in 7 ml anhydrous benzene was added 0.06 g magnesium and gradually, 1.17 g propionyl chloride. The next day the reaction mass was heated 1.5 hours at 80° and was treated as usual. 0.52 g of the propionate of 1-isopropyl-1-phenyl-3-dimethylaminopropanol-1, with b. p. 113-115° (1 mm) was obtained.

Found %: N 5.25, 5.32. $C_{17}H_{27}O_2N$. Calculated %: N 5.05.

The hydrochloride melted at 170-171° (from acetone).

Found %: N 4.37, 4.40. $C_{17}H_{28}O_2NCl$. Calculated %: N 4.46.

Acetate of 1-n-Butyl-1-phenyl-3-dimethylaminopropanol-1 (II, $R' = n\text{-}C_4H_9$, $R'' = R = CH_3$)

a) 1.2 g of acetyl chloride was added gradually to a solution of 3 g of 1-n-butyl-1-phenyl-3-dimethylaminopropanol-1 (m. p. 43-44°) in 5 ml of anhydrous acetone, with cooling to −7°. After half an hour, a colorless precipitate of 1-n-butyl-1-phenyl-3-dimethylaminopropanol-1 hydrochloride came down in a quantity of 2.74 g (68.5%). After recrystallization from a mixture of alcohol and ether, it melted at 162-163°.

Found %: N 4.37, 4.35. $C_{17}H_{28}O_2NCl$. Calculated %: N 4.46.

b) 2.5 g of the amino alcohol, 5 ml of acetic anhydride and 0.5 g of trichloroacetic acid in a solution of 15 ml of anhydrous benzene were used. The mixture was left for several days at room temperature, after which the solvents were removed at low vacuum. The reaction substance was acidified with hydrochloric acid, the neutral products were extracted with ether, the residue was treated with soda, and the oil which formed was extracted with ether. After drying and after removal of the ether, the residue was dissolved in anhydrous chloroform and the base was treated with dry hydrogen chloride until it had an acid reaction (Congo). After addition of the ether, 2.4 g of the acetate hydrochloride crystals with a m. p. of 162-163° (from acetone) was obtained, which gave no depression with the preceding form. The weight was 2.4 g (75%).

The Propionate of 1-n-Butyl-1-phenyl-3-dimethylaminopropanol-1 (II, R'=n-C_4H_9, R''=C_2H_5, R=CH_3)

2.22 ml of propionyl chloride was added gradually to a solution of 4.7 g of the amino alcohol in 7 ml of anhydrous acetone, with cooling with ice water. After half an hour, the colorless propionate hydrochloride precipitate came down. On the next day we heated the reaction substance for 1.5 hours at 50-60°; moreover, the precipitate dissolved, and was formed again on cooling. 3.9 g (60%) of the propionate hydrochloride of 1-n-butyl-1-phenyl-3-dimethylaminopropanol-1 was obtained, which, after recrystallization from a mixture of alcohol and ether, melted at 128-129°.

Found %: N 3.93, 4.02. $C_{18}H_{30}O_2NCl$. Calculated %: N 4.27.

The Benzoate of 1-n-Butyl-1-phenyl-3-dimethylaminopropanol-1 (II, R'=n-C_4H_9, R''=C_6H_5, R=CH_3)

0.4 g of metallic sodium was dispersed at 100-110° in 20 ml of dry dioxane; after cooling, 4.7 g of the amino alcohol was added, and the mixture was stirred at 100° for 4 hours. A small quantity of unreacted sodium was removed, and with cooling with ice, 3.09 g of benzoyl chloride was added dropwise. The reaction substance was heated for 2.5 hours on the plate, diluted with water (100 ml) and saturated with dry soda. The oil which formed was extracted with ether (200 ml), dried with sodium sulfate, and vacuum distilled. 3.5 g (56%) of the benzoate of 1-n-butyl-1-phenyl-3-dimethylaminopropanol-1 with a b. p. of 142-150° (0.5 mm) was obtained.

Found %: N 3.99, 3.86. $C_{22}H_{29}O_2N$. Calculated %: N 4.12.

The hydrochloride melted at 156-158° (from alcohol).

Found %: N 3.67, 4.03. $C_{22}H_{30}O_2NCl$. Calculated %: N 3.73.

The Acetate of 1-Isobutyl-1-phenyl-3-dimethylaminopropanol-1 (II, R'=iso-C_4H_9, R''=R=CH_3)

8 g of 1-isobutyl-1-phenyl-3-dimethylaminopropanol-1, 30 ml of anhydrous benzene, 0.4 g of magnesium and 6.4 g of acetyl chloride were used. On the next day the acetate hydrochloride precipitate which came down in a quantity of 9.5 g was filtered off, dissolved in water and treated with soda. The colorless oil which came to the surface was extracted several times with ether, dried with sodium sulfate and vacuum distilled. 6.4 g (68%) of the acetate of 1-isobutyl-1-phenyl-3-dimethylaminopropanol-1 with a b. p. of 122-123° (1.5 mm) was isolated.

Found %: N 5.27, 5.20. $C_{17}H_{27}O_2N$. Calculated %: N 5.05.

The hydrochloride melted at 172-173° (from alcohol).

Found %: N 4.60, 4.32. $C_{17}H_{28}O_2NCl$. Calculated %: N 4.46.

Dehydration of 1-Isobutyl-1-phenyl-3-dimethylaminopropanol-1. An attempt to carry out the acetylation of the amino alcohol under more severe conditions (with heating) led to its dehydration. A mixture of 8 g of the amino alcohol, 50 ml of anhydrous benzene, 0.4 g of magnesium and 6 g of acetyl chloride was heated at 85-90° for 10 hours. The oily precipitate which formed was converted to the base as usual and then to the hydrochloride. 2.7 g of the hydrochloride of the original amino alcohol with a m. p. of 172-173° was obtained. The solvents were removed from the filtrates, and the residue was dissolved in 5 ml of water and made alkaline with potash. The oil which came to the surface was extracted with ether, dried with sodium sulfate and vacuum distilled. 2.5 g of the dehydration product $(CH_3)_2CH-CH_2-C(C_6H_5)=CH-CH_2-N(CH_3)_2$ with a b. p. of 91-92.5° (1.5 mm) was obtained. Its hydrochloride melted at 181.5-182° (from a mixture of acetone and ether).

Found %: N 5.70, 5.55; Cl 13.62. $C_{15}H_{24}NCl$. Calculated %: N 5.47; Cl 13.86.

The Propionate of 1-Isobutyl-1-phenyl-3-dimethylaminopropanol-1 (II, R'=iso-C_4H_9, R''=C_2H_5, R=CH_3)

4.8 g of the amino alcohol, 0.26 g of magnesium, 15 ml of anhydrous benzene and 4.23 g of propionyl chloride were used. The mixture was heated for 2 hours at 85-90°, the benzene was removed at low vacuum, and the residue of the propionate hydrochloride was washed with anhydrous ether and dissolved in water. The aqueous solution was treated with soda, and the oil which formed was extracted with ether, dried with sodium sulfate and vacuum distilled. 4.8 g (78.5%) of the propionate of 1-isobutyl-1-phenyl-3-dimethylaminopropanol-1 with a b. p. of 116-118° (1.5 mm) was obtained.

Found %: N 4.52, 4.57. $C_{18}H_{29}O_2N$. Calculated %: N 4.82.

The oxalate melted at 165.5-166° (from alcohol). The iodomethylate melted at 180-181° (from alcohol).

The Benzoate of 1-Isobutyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = iso-C_4H_9, R'' = C_6H_5, R = CH_3)

5 g of the amino alcohol, 15 ml of anhydrous benzene, and 0.25 g of magnesium were used, and 6.98 g of benzoyl chloride was added gradually. After several minutes, the mixture evolved heat and then it was heated at 100° for 2 hours. After the usual treatment, 5.7 g (69%) of the benzoate of 1-isobutyl-1-phenyl-3-dimethylaminopropanol-1 with a b. p. of 154-157° was obtained (1.5 mm) as a heavy, viscous liquid.

Found %: N 4.14, 4.27. $C_{22}H_{29}O_2N$. Calculated %: N 4.13.

The oxalate melted at 170-171°.

The Phenoxyacetate of 1-Benzyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = $CH_2C_6H_5$, R'' = $CH_2OC_6H_5$, R = CH_3)

A solution of the acid chloride of phenoxyacetic acid in 3 ml of anhydrous ether was added slowly, with cooling with ice, to a solution of 2.73 g of 1-benzyl-1-phenyl-3-dimethylaminopropanol-1 (m. p. 70-72°) in 3 ml of anhydrous ether. An evolution of heat was observed, and all of the substance crystallized before long. The crystals were triturated twice with anhydrous ether and then were boiled in acetone to a constant melting point. 2.7 g of the phenoxyacetate hydrochloride of 1-benzyl-1-phenyl-3-dimethylaminopropanol-1 with a m. p. of 179-180° was obtained. 0.4 g more of the substance with a m. p. of 179-180° formed from the mother liquor. Its yield was 70%.

Found %: C 71.01, 70.86; H 6.52, 6.63; N 3.30, 3.24. $C_{26}H_{30}O_3NCl$. Calculated %: C 70.98; H 6.82; N 3.19.

The Cinnamate of 1-Benzyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = $CH_2C_6H_5$, R'' = $CH=CH-C_6H_5$, R = CH_3)

3 g of the acid chloride of cinnamic acid in 4 ml of benzene was added slowly, with cooling, to a solution of 3.2 g of the amino alcohol in 5 ml of anhydrous benzene. 2.05 g (0.45 g from the mother liquor) of the cinnamate hydrochloride of 1-benzyl-1-phenyl-3-dimethyl-1-aminopropanol-1 with a m. p. of 180-181° was obtained.

Found %: C 74.10, 74.00; H 7.30, 7.36; N 3.14, 3.15. $C_{27}H_{30}O_2NCl$. Calculated %: C 74.39; H 6.89; N 3.19.

The Hydrocinnamate of 1-Benzyl-1-phenyl-3-dimethylaminopropanol-1 (II, R' = $CH_2C_6H_5$, R'' = $CH_2CH_2C_6H_5$, R = CH_3)

2.9 g of the acid chloride of hydrocinnamic acid in 3 ml of benzene was added slowly, with cooling with ice, to a solution of 3.08 g of the amino alcohol in 4 ml of anhydrous benzene. Before long all of the substance had crystallized and was treated as described in the preceding experiment for obtaining phenoxyacetate. 2.22 g of the hydrocinnamate hydrochloride of 1-benzyl-1-phenyl-3-dimethylaminopropanol-1 with a m. p. of 141-142° was obtained.

Found %: C 74.04, 73.92; H 7.16, 7.62; N 3.13, 3.08. $C_{27}H_{32}O_2NCl$. Calculated %: C 74.05; H 7.31, N 3.20.

SUMMARY

1. 1-Alkyl-1-phenyl-3-dialkylaminopropanols-1 were synthesized in high yields by the action of Grignard reagents on β-dialkylaminopropiophenone hydrochlorides. Some of these amino alcohols were also obtained by the action of phenyllithium on aliphatic β-dialkylaminoethyl ketones.

2. 23 esters of 1-alkyl-1-phenyl-3-dialkylaminopropanols-1 were synthesized for the first time for the purpose of a pharmacological investigation. The highly water-soluble hydrochlorides of these esters were also obtained.

3. Some of the compounds synthesized underwent pharmacological testing and showed high physiological activity; the phenoxyacetate of 1-ethyl-1-phenyl-3-dimethylaminopropanol-1 was found to be a very powerful anesthetic with a relatively low toxicity.

4. The propionates (and also other esters) of 1-alkyl-1-phenyl-3-dialkylaminopropanols-1, the "discovered" analogs of promedol and other synthetic analgesics, had no sedative effect at all.

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INVESTIGATION IN THE FIELD OF VINYL ARYL ETHERS

III. COPOLYMERIZATION OF VINYL ARYL AND VINYL ALKYL ETHERS UNDER THE INFLUENCE OF IONIC CATALYSTS

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The ability of vinyl ethers to enter into a polymerization reaction is conditioned by the presence of the double bond in their molecule, the nature of which, however, is not the same for the vinyl alkyl and vinyl aryl ethers, since the electronic effect of the alkoxyl and aroxyl groups differ in their directions.

The fact that the vinyl alkyl and vinyl aryl ethers have the ability to react under the influence of ionic catalysts or radical initiators to a different degree, which to a known extent characterizes the reactivity of the compounds which we studied, is explained by this. The polymerization and copolymerization reactions of vinyl aryl ethers under the influence of ionic catalysts are a special case of the addition reactions which we studied earlier [1], and therefore, their study extends our information on the vinyl ethers.

The monomers of vinyl aryl and vinyl alkyl ethers have different chemical activities, depending chiefly on the reaction conditions. It is also known [2] that the activity of one monomer may be brought about by a second component present in the activated condition. A similar phenomenon also occurs in the production of vinyl aryl and alkyl ether joint polymers by polymerization under the influence of BF_3, without heating. In this instance, involvement of the vinyl aryl ether in the copolymerization occurs completely with activated molecules of vinyl alkyl ether, since with this kind of catalyst the vinyl aryl ethers do not polymerize without heating. It was shown earlier that with the assistance of ionic catalysts [3] the vinyl aryl ethers may polymerize and may copolymerize with vinyl alkyl ethers [4], and with esters of acrylic acid [5] under the influence of radical initiators. A logical extension of these works is the present report, devoted to the study of the joint polymerization reactions of vinyl aryl and vinyl alkyl ethers with the assistance of an ionic catalyst, BF_3 etherate.

The reaction mechanism of the vinyl ethers with ionic catalysts of the HX type, proposed by one of the authors [6], was based on the formation and decomposition of an oxonium complex $CH_2=CH-O\ldots HX$, giving an activated molecule $CH_3-\overset{+}{C}H-OR$, which was responsible for the polymerization.

There are two points ov view relative to the mechanism of the reaction of vinyl ethers with BF_3 [7]. According to the first, BF_3 may coordinate with a vinyl ether molecule in the OR-group (I) position, according to the second, it may coordinate in the vinyl group (II) position.

$$\begin{array}{l} CH_2::CH \\ \quad\quad | \\ F_3B:OR \end{array} \quad (I) \qquad\qquad \begin{array}{l} F_3B:CH_2:CH \\ \quad\quad\quad\quad | \\ \quad\quad\quad\quad :OR \end{array} \quad (II).$$

Recognizing the admissibility of both points of view, Formula (I) seemed to us more likely, corresponding to the character of the transformations of the vinyl ethers according to the ionic mechanism.

The general scheme of vinyl aryl and vinyl alkyl ether copolymers may have the following form:

$$CH_3-\underset{\underset{OAlk}{|}}{CH}-[-CH_2-\underset{\underset{OAr}{|}}{CH}-]_n-[-CH_2-\underset{\underset{OAlk}{|}}{CH}-]_{m-2}-CH=CH-OAlk.$$

We studied the joint polymerization of the vinyl aryl ethers for the following pairs of ethers: vinyl phenyl – vinyl n-butyl, vinyl phenyl – vinyl ethyl, and vinyl p-tert.-butylphenyl – vinyl n-butyl ethers.

An etherate of BF_3 as a 15% solution in ethyl ether, was used as the catalyst. The use of a solution of the etherate of BF_3 in dioxane as the catalyst gave the same polymerization effect as did the solution in ethyl ether. Our preference for the solution in ethyl ether is explained in that it is more stable and, in contrast to the solution in dioxane, may be kept unchanged for long periods. The copolymerization was carried out under different conditions without heating and by boiling in vacuo. The copolymerization, by boiling under atmospheric pressure, did not yield good results.

Because the ionic polymerization of vinyl aryl ethers (unlike vinyl alkyl ether) proceeds smoothly only on heating, in instances of the quantitative prevalence of vinyl aryl ether in the original mixture, we carried out the copolymerization by boiling in vacuo and, vice versa, polymerized mixtures of the original monomers, which contained a large fraction of vinyl alkyl ether, at room temperature. It is natural that the polymerization in vacuo is inevitably connected with losses of the more volatile monomer (vinyl alkyl ether). That only in the polymerization without heating, were able to obtain copolymers which corresponded in their composition to the composition of the original mixture of monomers, is accounted for by this.

The experiments showed that vinyl aryl ethers may enter into joint polymerization only at definite minimum concentrations of them in the mixture for given conditions. Otherwise, their inclusion does not occur, or it is very slight. Thus, without heating, vinyl phenyl ether at the original ratio of 1:6 and 1:3 to vinyl butyl ether is involved in copolymerization by only 1-3% (mole). It was also noted that, without heating, vinyl phenyl ether was included in copolymerization more difficultly than was vinyl p-tert.-butylphenyl ether, whereas the activities of these ethers were almost the same on copolymerization by boiling in vacuo. Comparing the ability of the vinyl alkyl ethers to be involved in the copolymerization of vinyl phenyl ether (without heating), it can be stated that vinyl ethyl ether at these ratios is more active than is vinyl butyl ether (Table 3).

Vinyl aryl and vinyl alkyl ether copolymers are sticky or viscously sticky, tacky, clear products, colorless or having a light-yellow color. It is known [3] that vinyl phenyl ether polymers are insoluble in alcohols. Their ability to dissolve in the alcohols corresponding to the vinyl alkyl ethers which enter into the composition of the copolymer, is a special characteristic of vinyl aryl and vinyl alkyl ether copolymers. This solubility decreases in proportion to the increase of the number of links of vinyl phenyl ether in the copolymer. The molecular weight and the viscosity of the vinyl aryl and alkyl ether copolymers occupies an intermediate position between those for the polyvinyl aryl and polyvinyl alkyl ethers; they decrease with an increase of the vinyl aryl content and increase with an increase of the vinyl alkyl ether contents. Fractionation [3] of the vinyl phenyl and n-butyl ether copolymers confirmed the relationship of the molecular weight to the copolymer composition (Table 3).

The vinyl aryl ether polymers and copolymers, on storage in a dessicator at room temperature, showed a considerable stability; moreover, no large change of the molecular weight, viscosity and appearance of odor and color occurred. The losses of weight on heating the copolymers at about 120° for 2 hours amounted to 5-6%; moreover, the molecular weight and viscosity did not change sharply.

EXPERIMENTAL *

The initial vinyl ethers had the constants listed in Table 1.

TABLE 1

Test no.	Ether	Boiling point	n_D^{20}	d_4^{20}
1	$CH_2=CH-OC_6H_5$	155-156°	1.5225	0.9770
2	$CH_2=CH-OC_6H_4C_4H_9$ (tert.)	219-220	1.5102	0.9332
3	$CH_2=CH-OC_2H_5$	36-36.5	1.3780	0.7530
4	$CH_2=CH-OC_4H_9$(n)	93-93.5	1.4020	0.7790

For brevity of reporting the experimental data, we present a description of only some of the experiments. Data for the remaining experiments are collected in Tables 2,3, and 4.

All of the copolymers obtained were treated with steam, dehydrated with benzene and dried to constant weight at 60° and 5 mm [3], after which their molecular weight (cryoscopically in benzene), the viscosity of a 1% solution in benzene (Ostwald viscometer) and elementary composition, were determined. Moreover, the copolymers were

* M. S. Egorova participated in carrying out the experiments.

tested for solubility in alcohols and in other organic solvents. Selective solubility in alcohols was an indication of the absence of vinyl aryl ether polymer (Table 4).

1. Joint polymerization of vinyl phenyl and vinyl ethyl ethers without heating. A mixture of 12.0 g (0.1 mole) of vinyl phenyl ether and 7.2 g (0.1 mole) of vinyl ethyl ether was placed in a three-necked flask, equipped with a thermometer, stirrer and reflux condenser. 3 drops of catalyst was introduced during 15 minutes, with stirring. The maximum temperature rise reached about 80°. After cooling, the catalyst was neutralized with ammonia, and the polymer was treated as usual [3]. 16.43 g (85.4%) of a light, viscous product, which was soluble in butyl and ethyl alcohols and insoluble in methyl alcohol, was isolated. See Table 2 for the properties and composition of the resulting copolymer.

TABLE 2

Original ethers	Reaction conditions	Ratio of ethers used (in moles)	Per cent of BF_3 etherate	Copolymer yield (in %)	M	Viscosity (in centi poises)	Elementary analysis (in %)		Ratio of vinyl aryl ether to vinyl alkyl in copolymer (in mole %)
							C	H	
Vinyl phenyl and vinyl ethyl	without heating	0:1	0.006	94.5	7644	1.1190	66.63	11.18	0:100
		1:6	0.030	71.0	2426	0.8313	66.58	10.87	0:100
		1:2	0.030	62.3	1557	0.7646	69.11	10.64	11.7:88.3
		1:1	0.040	85.4	697.0	0.7116	74.73	8.68	47.9:52.1
	boiling in vacuo	1:1	0.040	42.0	337.0	0.6963	80.20	6.68	100.0:0
Vinyl phenyl and vinyl butyl	without heating	1:1	0.036	76.3	7663	1.4350	71.92	12.07	0:100
		1:6	0.010	58.6	5397	0.8568	72.17	11.75	1.3:98.7
		1:3	0.034	71.4	2391	0.7534	72.31	11.90	2.6:97.4
		1:1.2	0.070	62.8	1676	0.7408	72.92	11.65	9.1:90.9
		1:2	0.080	48.5	1434	–	73.58	11.19	16.4:83.6
		1:1	0.096	67.0	624.0	0.7200	75.47	9.68	38.1:61.9
	boiling in vacuo	1:1	0.073	47.0	472.0	0.7164	78.66	7.72	79.7:20.3
		2:1	0.070	62.0	409.0	0.7039	79.14	7.34	86.6:13.4
		3:1	0.070	60.3	374.0	0.6998	80.23	7.47	100:0
		1:0	0.080	80.5	352.0	0.6961	79.97	6.72	100.0:0
Vinyl p-tert.-butylphenyl and vinyl butyl	without boiling	1:3	0.070	70.0	1278	0.7485	73.48	11.54	8.8:91.2
		1:3	0.070	82.0	989.0	0.7302	74.80	11.10	18.1:81.9
		at(78°)							
		1:1	0.200	88.0	684.0	0.7074	78.05	10.14	47.2:52.8
	boiling in vacuo	1:1	0.130	42.0	511.0	0.6984	80.50	9.71	77.9:22.1
		1:0	0.065	86.7	455.0	0.7082	81.77	9.15	100:0 (m. p. 40-41°)

2. Joint polymerization of vinyl phenyl and vinyl butyl ethers by boiling in vacuo. 12.0 g (0.1 mole) of vinyl phenyl ether and 10.0 g (0.1 mole) of vinyl butyl ether were placed in a round-bottomed flask, equipped with a reflux condenser, thermometer and capillary. The flask was heated on the water bath until the reaction mixture boiled. At 37° and 26 mm, 5 drops of catalyst was introduced into the flask, which caused an increase of the temperature to about 93° at 17 mm. After the usual treatment of the polymer, 10.3 g of the light, viscous copolymer which was soluble in butyl alcohol and insoluble in ethyl and methyl alcohols, was isolated. The properties and composition of the copolymer are cited in Table 2.

The properties of one of the vinyl phenyl ether copolymers and its fractions are given in Table 3.

3. Joint polymerization of vinyl p-tert.-butylphenyl and vinyl n-butyl ethers. A mixture of 15.75 g of vinyl p-tert.-butylphenyl ether and 8.75 g of vinyl n-butyl ether was placed in a flask under the conditions of the experiment described above. 9 drops of catalyst was introduced during 5 minutes, which caused a gradual increase of the temperature of the mixture to about 83°. On completion of the polymerization, the polymer was subjected to the

usual treatment and dried in vacuo. 22.0 g (88%) of a clear, yellow, viscous product was isolated. The resulting copolymer dissolved in butyl alcohol and did not dissolve in ethyl and methyl alcohols. The properties and composition of the copolymer are cited in Table 2.

TABLE 3

Copolymer	Yield (in %)	M	Viscosity (in centipoises)	Elementary analysis (in %)		Ratio of vinyl phenyl ether to vinyl alkyl in the copolymer (in mole %)
				C	H	
Obtained in molar ratio of 1:1.2	78.0	674	0.7348	75.86	9.14	43.0:57.0
1st fraction	36.0	2415	0.7491	74.00	11.05	21.1:78.9
2nd fraction	45.0	380	0.6996	78.32	7.65	75.0:25.0

TABLE 4

Test no.	Solvent	Vinyl phenyl ether polymer	Vinyl phenyl and vinyl butyl ether copolymer	Vinyl butyl ether polymer	Vinyl phenyl and vinyl ethyl ether copolymer	Vinyl ethyl ether polymer	Vinyl p-tert.-butyl-phenyl ether polymer	Vinyl p-tert.-butyl-phenyl and vinyl butyl ether copolymer
1	Acetone	++	++	+	++	++	++	+
2	Butyl alcohol	−	++	++	++	++	++	++
3	Ethyl alcohol	−	−	−	++	++	−	−
4	Methyl alcohol	−	−	−	−	+	−	−
5	Acetic acid	+	++	++	++	++	++	++
6	Gasoline	+	+	++	+	++	++	++

Note. In Table 4 the following symbols are designated: ++ soluble; − insoluble; + partially soluble. The polymers and copolymers presented were soluble in benzene, toluene, dioxane, ethyl ether, ethyl acetate and vinyl ethers. Since the solubility of the copolymers, besides the molecular weights, depends also on their vinyl aryl ether contents, copolymers with close vinyl aryl ether contents were used in the tables.

SUMMARY

1. The conditions of involving vinyl aryl ethers in copolymerization with vinyl alkyl ether under the influence of BF_3 etherate were determined.

2. Vinyl aryl and vinyl alkyl ether copolymers with different vinyl aryl ether contents were obtained. The copolymers formed were characterized and tested for solubility and for certain physical properties.

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DECOMPOSITION OF ESTERS OF BENZOIC ACID OVER A CHROMIUM CATALYST

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In the literature it is customarily assumed that esters are the intermediate compounds in the process of the ketonization of primary aliphatic alcohols. In a series of works [1-5] the presence of esters and of aldehydes was detected in the products of the transformation of these alcohols over copper or chromium catalysts. On passage of aliphatic esters over the latter, high yields of the corresponding ketones are attained (about 50% and above, based on the initial ester). This, as will be indicated, is the basis of the following consecutive transformations: alcohol → aldehyde → ester → ketone.

In the literature, almost no light is thrown on the transformation of aromatic series esters. Sabatier and Mailhe [6] indicated that benzoic acid and ethylene are the sole products of the decomposition of ethyl benzoate over thorium oxide at 400° and above. We set ourselves the problems of studying the decomposition reaction of benzoates, and of selecting the conditions which favor their conversion to ketones over a zinc-chromium catalyst, which, for the aliphatic esters, gave high yields of ketones [1, 2]. Experiments were carried out in the presence of additionally introduced hydrogen (2 liters per hour) which, as experiments previously carried out showed, in all cases had a favorable effect, increasing the ketone yields and protecting the catalyst from deactivation [2,3,4].

Three benzoates, ethyl, n-butyl and isoamyl, were used as objects of the investigation. The conditions and results of the experiments are given in Tables 1, 2 and 3, from the data of which it is evident that at 380° the percentage conversion of the esters is rather low. In proportion to a further increase of temperature, the yields of benzene and the content of CO_2 and olefin in the gas increased strongly, and benzoic acid was invariably present in the residues from the distillation of the condensate. This shows that to a great extent the decomposition of the benzoates takes place according to the scheme of Sabatier and Mailhe [6]:

$$C_6H_5COOC_nH_{2n+1} \longrightarrow \begin{matrix} C_6H_5COOH + C_nH_{2n}. \\ \downarrow \\ C_6H_6 + CO_2 \end{matrix}$$

However, parallel with these reactions proceeded processes which led to the formation of the mixed ketones, acetophenone, butyrophenone and valerophenone, the yields of which under optimum conditions are small, amounting to 9.3, 6.6 and 2.3%, respectively. The symmetrical ketone, benzophenone, was not detected in the reaction products. It was noted that an increase of the molecular weight of the ester necessitated an increase of reaction temperature, which resulted in the lowering of the ketone yields and the increase of benzene. The aliphatic-aromatic ketones formed best at 400-420° and at a volume rate of 50-60. Above 420° the benzene yields increased considerably and the ketone yields were reduced. A decrease of the volume rate to 20-30 brought about an increase of the benzene yields, and its increase to 80-100 reduced the percentage conversion of the esters because of the brief contacting time.

The presence of benzaldehyde and aliphatic esters (ethyl acetate in the decomposition of ethyl benzoate, butyl butyrate in the decomposition of butyl benzoate) in the reaction products, and the presence of CO in the gas, enabled us to assume that the formation of ketones from benzoates takes place via their intermediate decomposition to aldehydes, followed by conversion of the latter to ketones, possibly by the aldol mechanism.

For example, the formation of acetophenone from ethyl benzoate must proceed according to the scheme:

$$C_6H_5COOC_2H_5 \longrightarrow C_6H_5CHO + CH_3CHO,$$

$$C_6H_5CHO + CH_3CHO \longrightarrow C_6H_5CHOHCH_2CHO \xrightarrow{-CO} C_6H_5CHOHCH_3 \xrightarrow{-H_2} C_6H_5COCH_3,$$

$$\text{i. e., overall: } C_6H_5COOC_2H_5 \longrightarrow C_6H_5COCH_3 + CO + H_2.$$

The formation of butyrophenone from butyl benzoate and isovalerophenone from isoamyl benzoate proceed similarly.

TABLE 1

Decomposition of Ethyl Benzoate

Temperature	Volume rate	Yields in percentages of initial ester (from analysis of fractions)				Gas composition (in volume %)				
		Benzene	Benzaldehyde	Acetophenone	Unaltered benzoate	CO_2	C_nH_{2n}	CO	H_2	Residue
380°	50	3.0	3.4	8.1	64.6	–	–	–	–	–
400	45	6.1	5.4	9.3	18.1	18.7	9.7	0.7	61.1	9.8
400	20	24.1	1.4	4.0	3.9	26.8	17.3	9.8	42.8	3.3
400	80	6.6	3.6	5.4	29.3	24.1	17.4	5.1	49.0	4.4
420	75	13.4	3.1	8.1	8.4	–	–	–	–	–
450	40	33.4	0.6	1.4	0.8	30.6	20.1	14.8	30.0	4.5

TABLE 2

Decomposition of Butyl Benzoate

Temperature	Volume rate	Yields in percentages of initial ester (from analysis of fractions)					Gas composition (in volume %)				
		Benzene	Benzaldehyde	Butyrophenone	Butyl butyrate	unaltered butyl benzoate	CO_2	C_nH_{2n}	CO	H_2	Residue
380°	60	0.0	0.0	0.0	0.0	95.0	2.0	4.7	1.7	91.6	–
400	60	4.7	7.0	4.2	0.5	64.0	22.2	13.6	1.9	59.5	2.8
420	25	14.8	4.3	1.2	0.0	49.0	17.5	9.5	3.9	69.1	–
420	55	18.6	1.1	5.8	0.7	12.0	20.6	13.2	17.0	49.2	–
420	80	4.8	0.9	6.6	0.0	83.4	23.6	13.8	3.0	59.6	–
420	100	0.0	0.0	4.2	0.0	80.6	–	–	–	–	–
440	50	24.8	0.6	1.0	0.6	7.5	17.7	17.1	25.0	40.2	–

TABLE 3

Decomposition of Isoamyl Benzoate

Temperature	Volume rate	Yields in percentages of initial ester (from analysis of fractions)					Gas composition from experiments (in volume %)				
		Isoamylene	Benzene	Benzaldehyde	Isovalerophenone	unaltered Isoamyl benzoate	CO_2	C_nH_{2n}	CO	H_2	Residue
400°	40	–	6.4	0.0	2.3	73.4	10.7	7.4	3.7	78.2	–
420	40	6.8	15.9	3.7	2.3	70.7	10.8	11.6	5.0	72.6	–
440	55	6.6	17.5	1.1	2.2	28.1	27.0	18.0	19.0	36.0	–
460	55	7.6	26.4	0.3	0.2	24.2	15.1	18.6	30.1	36.2	–

A confirmation of the validity of such a ketonization mechanism is also the result of the experiments with benzyl acetate, which is matameric with respect to ethyl benzoate, and which at 400° and at a volume rate of 50, i. e., under optimum conditions for the formation of acetophenone from ethyl benzoate, gave a condensate with 4.5% acetone, 4.3% acetophenone, 11.1% benzaldehyde and 1.9% ethyl acetate, i. e., the same products as the metameric ethyl benzoate.

On decomposition of the benzoates, especially at high temperatures (420-460°), a large quantity of carbon monoxide (about 20-30%) was detected in the gas, which may be attributed to the decomposition of benzaldehyde according to the well-known reaction [7]: $C_6H_5CHO \longrightarrow C_6H_6 + CO$. The results obtained enabled us to assume that, over copper or chromium-containing catalysts, the conversion mechanism of primary alcohols is different at different temperatures. At low temperatures (for example, 250-270°, for copper catalysts) the reaction stops with the formation of the corresponding esters; with an increase of the temperature to about 325-350° symmetrical ketones with (2n−1)

carbon atoms are obtained from the initial $C_nH_{2n+1}OH$, but not according to the Sabatier-Kagan mechanism. At 325-350° the dissociation of the esters into two aldehyde molecules occurs, from which ketones form, probably according to the aldol mechanism, in favor of which are the considerable quantities of CO which form during the reaction. The process may be represented by the overall scheme:

$$2RCH_2CH_2OH \xrightleftharpoons{-4H} 2RCH_2CHO \underset{> 325°}{\overset{< 325°}{\rightleftharpoons}} RCH_2COOCH_2CH_2R$$

$$RCH_2CHOHCHRCHO \xrightarrow{-CO} RCH_2CHOHCH_2R \xrightarrow{-2H} RCH_2COCH_2R.$$

The structures of the ketones obtained on decomposition of the metameric esters favors such transformations, since it is impossible to account for their formation by any other method. The absence of benzophenone in the reaction products is especially convincing, since the benzaldehyde obtained by the decomposition of benzoates cannot undergo aldolization, but can be condensed to benzyl benzoate, which in the event of the validity of the Sabatier-Kagan mechanism, must yield benzophenone as the chief reaction product. The complete absence of the latter clearly indicated the aldol mechanism of formation of ketones from esters and, consequently, from alcohols.

EXPERIMENTAL

The apparatus, procedure for the catalytic experiments, and analysis of the reaction products described earlier in [4] were used for carrying out the experiments.

Experiments on Decomposition of Ethyl Benzoate*

Ethyl benzoate having the following constants was used for the work:

B. p. 209-212°, n_D^{20} 1.5060, d_4^{20} 1.0504.

Literature values: b. p. 213.2°, d_4^{15} 1.0509, n_D^{20} 1.506

The following fractions were obtained by the fractionation of the catalyzates: 1st 78-100°, 2nd 100-175°, 3rd 175-205°, 4th 205-210°, and residue. After carrying out analyses, the fractions of similar boiling point from all the distillations were combined and redistilled from a fractionating column, for the purpose of separation of the individual substances and of their identification.

The 1st fraction contained chiefly benzene, which was isolated and identified:

B. p 80.5-81.0°, d_4^{20} 0.8793, n_D^{20} 1.5004.

Literature values: b. p. 80.1°, d_4^{20} 0.87895, n_D^{20} 1.50124.

The 2nd fraction was an intermediate fraction and consisted of no more than 2-3% by weight of condensates and contained a certain quantity of benzaldehyde.

According to analyses, the 3rd fraction contained benzaldehyde, acetophenone and unreacted ethyl benzoate. By a second distillation, a 202-208° fraction was isolated, which corresponded to acetophenone, from which a semicarbazone of m. p. 196° was prepared (after recrystallization from 30% ethanol), the m. p. of which, according to the literature, was 198°.

Found %: N 24.22. $C_9H_{11}ON_3$. Calculated %: N 23.72.

Obviously, on long storage the benzaldehyde included in the 3rd fraction oxidized to benzoic acid, which was also detected on redistillation (sublimed).

The 4th fraction was the almost pure original ethyl benzoate.

The residue contained unreacted ester, and also benzoic acid which was isolated by extraction with hot water. After recrystallization from hot water, the benzoic acid had a m. p. of 121-122° (121.4° according to the literature); a test of a mixture with known benzoic acid gave no melting point depression.

Experiments on Decomposition of Butyl Benzoate

The initial ester was prepared by a 6-hour boiling of benzoic acid and by dehydration of the butyl alcohol

* V. B. Lushchik carried out the first experiments on the decomposition of ethyl benzoate.

with concentrated H_2SO_4. After freeing of the resulting ester from sulfur compounds by boiling with mercuric acetate and by redistillation, it had the following constants:

B. p 247-249°, d_4^{20} 1.010, n_D^{20} 1.4930.

Literature values: b. p. 250.3°, d_{15}^{15} 1.0111, n_D^{20} 1.4930.

The following fractions were obtained by distillation of the condensates from the experiments: 1st 72-76°, 2nd 76-87°, 3rd 87-205°, 4th 205-242°, 5th 242-253°, and residue.

According to analyses, the 1st fraction contained a small amount of an aldehyde, apparently butyraldehyde.

The 2nd fraction was redistilled, and a fraction of pure benzene was obtained:

B. p 80.8-81.0°, d_4^{20} 0.8777, n_D^{20} 1.4996.

According to the analyses, the 3rd fraction contained benzaldehyde, butyl butyrate and butyrophenone.

The 4th fraction was redistilled. From the 225-235° fraction which was obtained a semicarbazone was prepared, which after recrystallization from ethanol had a m. p. of 184.5-185.0° (the literature value for butyrophenone semicarbazone was 187°).

Found %: N 20.27, 20.59. $C_{11}H_{15}ON_3$. Calculated %: N 20.47.

The 5th fraction was unreacted butyl benzoate, which was separated by redistillation:

B. p. 252-253°, d_4^{20} 1.0108, n_D^{20} 1.5012.

Besides the original unreacted ester, the residue contained benzoic acid, which was isolated by extraction with hot water and purified by sublimation (m. p. 121-122°, 121.4° according to the literature); a test of a mixture with known benzoic acid gave no melting point depression.

Experiments on Decomposition of Isoamyl Benzoate

The initial ester, prepared in the same way as butyl benzoate, had the following constants:

B. p. 96-98° (4 mm), d_4^{20} 0.9873, n_D^{20} 1.4949.

Literature values: b. p. 262.3°, 104.5° (5 mm), d_{4}^{4} 0.9925, n_D^{20} 1.4950.

The following fractions were obtained by the distillation of the condensates from the experiments: 1st 20-24°, 2nd 78-84°, 3rd 84-179°, 4th 179°-245°, 5th 245-253°, and residue.

The 1st fraction was isoamylene (its b. p. is 21° according to the literature); it decolorized bromine water instantly.

The 2nd fraction was almost pure benzene, which, after redistillation, had the following constants:

B. p. 80.8-81.0°, d_4^{20} 0.8787, n_D^{20} 1.4993.

According to analyses, the 3rd fraction contained benzaldehyde and a ketone, probably diisobutyl ketone (its b. p. is 168°, according to the literature).

The 4th fraction, included in small quantities, was an intermediate fraction, and according to analyses contained benzaldehyde, isovalerophenone and unreacted isoamyl benzoate.

The 5th fraction was redistilled, whereupon a 210-240° and a 255-260° fraction were separated.

From the 210-240° fraction, a semicarbazone having a m. p. of 207° (according to the literature, isovalerophenone semicarbazone has a m. p. of 209°) was prepared in a very small quantity.

The 255-260° fraction was unreacted isoamyl benzoate:

B. p. 255-260°, d_4^{20} 0.9961, n_D^{20} 1.4932.

The residue contained benzoic acid, which was extracted with hot water and was purified by sublimation, after which it had a m. p. of 121-122°; a test of a mixture with known benzoic acid gave no melting point depression.

SUMMARY

1. On passage over a zinc-chromium catalyst, benzoates (ethyl, butyl and isoamyl) were transformed in two directions, forming benzene, CO_2 and an olefin, on the one hand, and an aliphatic-aromatic ketone, on the other.

2. A temperature of 400-420° and a volume rate of 50-60 were optimum conditions for the formation of aliphatic-aromatic ketones. The yield of acetophenone was 9.3%, of butyrophenone 6.6% and of isovalerophenone 2.3%, based on the original ester.

3. The ketonization of benzoates apparently takes place via their intermediate decomposition to aldehydes, followed by condensations according to the aldol scheme.

4. The decomposition of aromatic esters to ketones over zinc-chromium catalysts proceeds much more difficultly than does that of aliphatic esters.

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* T. p. = C. B. Translation pagination.

COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

XIV. REACTION OF SOME ETHYL ESTERS OF β-MONOALKYL-SUBSTITUTED GLYCIDIC ACIDS WITH ANILINE

V. F. Martynov and G. Olman

The question as to where rupture of the oxide ring occurs in the reaction of ethyl esters of β,β'-dialkyl-substituted glycidic acids with various aromatic amines was studied in a number of preceding papers [1-5]; in this connection it was shown that in all of the investigated cases the rupture of the oxide ring occurs at the β-carbon atom. Simultaneously with obtaining an answer to this problem a new method was developed for the synthesis of 2,3-dialkyl-substituted indoles.

Here the question naturally arose as to whether the ethyl esters of the β-monoalkyl-substituted glycidic acids would also obey the discovered rules. The elucidation of this problem was also of interest for the reason that it might lead to a new method for the synthesis of the 2-alkyl-substituted indoles, which compounds are obtained with considerable difficulty by presently known methods.

We prepared the starting β-alkyl-substituted glycidic acids by the Darzens method [6], which method consists in the condensation of aldehydes with ethyl monochloroacetate in the presence of sodium ethylate. With this method of preparation the yields of the glycidates, as a rule, were small (20-30%). This, evidently, is explained first of all by the much faster polymerization rate of the aldehydes when compared with their condensation rate with the chloroacetic ester. This tendency to undergo polymerization is especially pronounced for the lower aldehydes, for which reason we were unable to synthesize the simplest ethyl β-methylglycidate and proceeded in our work from the more complex aldehydes, the tendency of which to polymerize, as is known, is much more weakly expressed.

We obtained four new ethyl glycidates,* namely, the ethyl esters of β-proplyglycidic, β-isopropylglycidic, β-isobutylglycidic and β-hexylglycidic acids. The formulas of these esters are given in the Table. In synthesizing these esters we used diethyl ether as the solvent, which increased the yields of the glycidates from 20-30 to 40%.

Investigation revealed that the glycidates differ sharply in their reactivity with aniline. The esters possessing a straight-chain radical in the β-position are the most reactive.

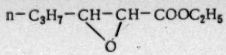
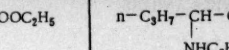
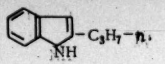
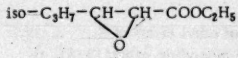
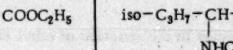
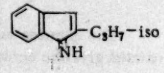
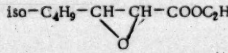
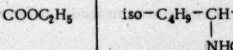
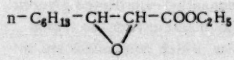
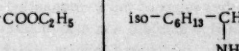
The reaction proceeds with especial ease and without any reaction by-products for the ethyl ester of β-propylglycidic acid. For the β-hexylglycidic ester the activity toward aniline drops, but the reaction still proceeds with fairly good yield. On passing to the glycidates that have a branched-chain radical the reactivity of the oxide ring is sharply reduced, which reduction is the more marked the closer the branched-chain portion of the radical is located to the oxide ring. Simultaneously with this an increase in the reactivity of the ester grouping toward aniline is observed, i.e., a tendency to form anilides. The latter property is so sharply expressed for the ethyl esters of β-isopropyl- and isobutylglycidic acids that the synthesis of the corresponding aniline addition products to the oxide ring in the pure form is almost impossible, always the anilide is present as impurity.

All of these behavior characteristics of the ethyl glycidates can be explained by steric hindrance factors, originating at the oxide ring. The larger the radical in the case of the straight chains or the closer the branched chain is to the oxide ring, the greater is the steric hindrance and the weaker is the tendency for addition reactions at the oxide ring.

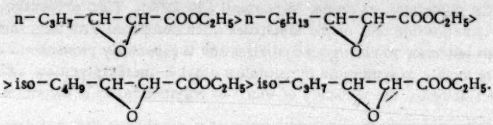
On the basis of our obtained data, given in the Table, the studied β-monoalkyl-substituted glycidic acid esters can be arranged in the following order of decreasing reactivity of the oxide ring with aniline:

* It is true that Darzens [7] mentions obtaining the indicated glycidates, but he fails to give any constants for them.

TABLE

Ethyl Ester of the Glycidic Acid	Addition Product	Time of Heating, Temperature, and Yield in %	Indole Derivative
		6 hours 150–155°, 67.5	
		15 hours 134–135°, 28.5	
		10 hours 145–150°, 33.1	
		6 hours 145–155°, 41	

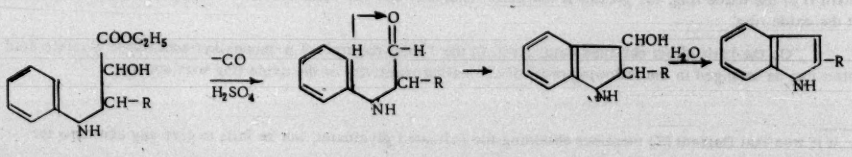
* The anilide was also isolated, cf. Experimental Part.



The question as to where the oxide ring of the investigated glycidic acid esters is ruptured under the influence of aniline was answered by the same method that was previously used by us for a similar purpose in the case of the β,β'-dialkyl-substituted glycidic acids [1-5]. This method is based on the fact that the esters of α-hydroxy-β-arylamino acids when reacted with concentrated sulfuric acid cleave carbon monoxide and form 2,3-dialkyl-substituted indoles. In the present case, if the esters of the β-monoalkyl-substituted glycidic acids react with aniline by the same rule as do the disubstituted glycidic acid esters, i.e. with rupture of the oxide ring at the β-carbon atom and the formation of α-hydroxy-β-arylamino acid esters, then they also should be decomposed in exactly the same manner under the influence of concentrated sulfuric acid with the evolution of carbon monoxide and the formation of the corresponding indole.

Actually, all of the compounds obtained by us in the addition of aniline to the glycidic acid esters under the influence of concentrated sulfuric acid reacted with the evolution of copious amounts of carbon monoxide. This was indisputable evidence that in the present case also we are dealing with the esters of α-hydroxy-β-arylamino acids. For conclusive proof it was necessary for us to isolate the corresponding indoles.

From the very nature of the reaction for the decomposition of α-hydroxy-β-alkyl-β-anilinopropionic acid esters under the influence of H_2SO_4 we should obtain the 2-alkyl-substituted indoles. In general form this reaction can be depicted as follows:



Actually, from the two addition products of aniline with the glycidates (the ethyl ester of α-hydroxy-β-anilinocaproic acid and the ethyl ester of α-hydroxy-β-anilinoisocaproic acid) after the decomposition reaction with sulfuric acid we were able to isolate the corresponding indoles: 2-propylindole and 2-isopropylindole. The 2-propylindole was obtained by the French scientists, who give a m.p. of 34° for it [8]. The melting point of our product was 33-34°.

We were unable to go from the addition products of aniline with the other two glycidates to the indoles for the reason that we had extremely minute amounts of the starting products at our disposal. In the case of the ethyl ester of α-hydroxy-β-anilinoisoenanthic acid we were only able to isolate the red picrate of the corresponding indole, m.p. 91-92°.

EXPERIMENTAL

Synthesis of Ethyl β-Propylglycidate. The compound was synthesized by the Darzens method [6]. To a mixture of 72 g (1 mole) of freshly distilled butyraldehyde and 122.5 g (1 mole) of ethyl monochloroacetate was added in small portions 1 mole of sodium ethylate at such a rate that the temperature remained below 0°. After the usual treatment for this method there was obtained 32.4 g (20.5%) of ethyl β-propylglycidate.

(1) B.p. 97–98° at 19 mm, d_4^{20} 0.9789, n_D^{20} 1.4327, MR_D 41.94; calc. 40.37; EM 1.57.

Found %: C 61.20; H 8.76. $C_8H_{14}O_3$. Calculated %: C 60.80; H 8.85.

Synthesis of Ethyl α-Hydroxy-β-anilinocaproate. A mixture of 15.4 g (0.097 mole) of ethyl β-propylglycidate and 27 g of aniline (0.34 mole) was heated in a sealed ampul for 6 hours at 150-155°. Distillation of the mixture gave 16.8 g (67.5%) of viscous, yellowish liquid.

(2) B.p. 131.5–132° at 0.5 mm, d_4^{20} 1.0696, n_D^{20} 1.5264, MR_D 72.09; calc. 68.93; EM_D 3.15.

Found %: N 5.73. $C_{14}H_{21}O_3N$. Calculated %: N 5.58.

Conversion of Ethyl α-Hydroxy-β-anilinocaproate into 2-Propylindole. A mixture of 3.6 g of ethyl α-hydroxy-β-anilinocaproate and 25 ml of concentrated sulfuric acid was heated on the hot plate under constant stirring with a thermometer immersed in the liquid. The evolution of carbon monoxide bubbles began at 95°, which became very intense at 115°. The gas evolution continued for about 30 minutes, during which time the reaction mixture became dark-red in color.

After the cessation of gas evolution the mixture was poured over ice to give a dark-yellow emulsion. After the acid had been neutralized with alkali the whole mixture was steam-distilled. The distillate was extracted with ether, the ether distilled off, and the residual yellow liquid vacuum-distilled. The yield of viscous yellow liquid with b.p. 119-120° at 1 mm was 1.1 g (50%), which liquid crystallized on standing. After recrystallization from aqueous alcohol, m.p. 33-34°.

(1) Found %: N 8.81 $C_{11}H_{13}N$. Calculated %: N 8.80.

Picrate: red needlelike crystals, m.p. 144-145°. (with decompn.)

Synthesis of Ethyl β-Isopropylglycidate. To a mixture of 72 g of freshly distilled isobutyraldehyde, 122.5 g of ethyl monochloroacetate and 500 ml of dry ether was added in small portions 1 mole of sodium ethylate. Here the temperature was not allowed to rise above 0°. After the usual treatment there was obtained 60 g (38%) of ethyl β-isopropylglycidate.

(2) B.p. 86–87.5° at 13 mm; d_4^{20} 1.0024, n_D^{20} 1.4313, MR_D 40.81; calc. 40.37; EM_D 0.44.

Found %: C 60.25; H 8.65. $C_8H_{14}O_3$. Calculated %: C 60.80; H 8.85.

Synthesis of Ethyl α-Hydroxy-β-anilinoisocaproate. A mixture of 20 g (0.32 mole) of ethyl β-isopropylglycidate and 36 g (0.37 mole) of aniline in a sealed ampul was heated for 15 hours in an oil thermostat at 134-135°, where the mixture turned slightly yellow. The reaction products were vacuum-distilled. There was isolated 9 g (28%) of viscous yellowish liquid with b.p. 120-125° at 0.5 mm, which later crystallized. After recrystallization from petroleum ether, white crystals with m.p. 69°.

(3) Found %: N 5.86. $C_{14}H_{21}O_3N$. Calculated %: N 5.58.

In the interval of 160-170° at 0.5 mm there distilled 1.5 g of the anilide of α-hydroxy-β-anilinoisocaproic acid as a viscous yellow mass, which immediately crystallized in the outlet tube of the distilling flask. The

crystals were washed with ether, in which they are insoluble. M.p. 133.5°.

(4) Found %: N 9.62. $C_{18}H_{22}O_2N_2$. Calculated %: N 9.42.

Conversion of Ethyl α-Hydroxy-β-anilinoisocaproate into 2-Isopropylindole. A mixture of 1.5 g of ethyl α-hydroxy-β-anilinoisocaproate and 10 ml of concentrated sulfuric acid was heated with stirring to 135°.

For about 30 minutes the evolution of carbon monoxide was quite intense. Then the reaction mixture was poured over ice to give a crystalline precipitate. Weight 0.5 g (52%). Recrystallization from aqueous alcohol gave glistening while leaflets with m.p. 73.5°.

(5) Found %: N 8.58. $C_{11}H_{13}N$. Calculated %: N 8.78.

Picrate: red needlelike crystals with m.p. 120° (with decompn.).

Synthesis of Ethyl β-Isobutylglycidate. This glycidate was synthesized in the same manner as the β-isopropylglycidate. For reaction there was taken 43 g (0.5 mole) of freshly-distilled isovaleraldehyde, 61.5 g (0.5 mole) of ethyl monochloroacetate, 0.5 mole of sodium ethylate and 500 ml of diethyl ether. The yield of ethyl β-isobutylglycidate was 31 g (36%).

(1) B.p. 105–106° at 12 mm, d_4^{20} 0.9936, n_D^{20} 1.4396, MR_D 45.60; calc. 44.99; EM_D 0.61.

Found %: C 63.35; H 9.32. $C_9H_{16}O_3$. Calculated %: C 62.80; H 9.8.

Synthesis of Ethyl α-Hydroxy-β-anilinoisoenanthoate. A mixture of 10 g of ethyl β-isobutylglycidate and 27 g of aniline in a sealed ampul was heated for 10 hours at 145-155°. Two fractions were obtained when the reaction mixture was vacuum-distilled. The first fraction with b.p. 125-130° at 0.5 mm and weighing 5.1 g (33.1%) was ethyl α-hydroxy-β-anilinoisoenanthoate. The substance crystallized. After recrystallization from petroleum ether, m.p. 63-63.5°.

(2) Found %: N 5.58. $C_{14}H_{23}O_3N$. Calculated %: N 5.53.

The second fraction with b.p. 180-190° at 0.5 mm, probably the anilide of α-hydroxy-β-anilinoisoenanthic acid, weighed 1.2 g. The substance crystallized during distillation. After pruification with benzene, m.p. 187-188° (with decompn.).

Synthesis of Ethyl β-Hexylglycidate. The synthesis was run in the same manner as described above for the other glycidates. For reaction there was taken 42 g of enanthaldehyde, 45.5 g of ethyl monochloroacetate, 25 g of sodium ethylate and 300 ml of diethyl ether. The yield of the hexylglycidate was 17 g (23.5%).

(3) B.p. 117–119° at 6 mm, d_4^{20} 0.9882, n_D^{20} 1.4448, MR_D 53.84; calc. 54.22

Synthesis of Ethyl α-Hydroxy-β-anilinopelargonate. A mixture of 10 g of ethyl β-hexylglycidate and 24 g of aniline in a sealed ampul was heated for 6 hours at 145-155°. The reaction mixture became viscous and acquired a yellow color. Vacuum-distillation gave 6 g (41%) of a fraction with b.p. 153-155° at 0.5 mm.

(4) Found %: N 4.88. $C_{17}H_{27}O_3N$. Calculated %: N 4.78.

SUMMARY

1. The reaction of aniline with the ethyl esters of β-propyl-, β-isopropyl-, β-isobutyl- and β-hexylglycidic acids was studied. It was established that the oxide ring of the indicated glycidic acids is opened at the β-carbon atom. The new ethyl esters of the glycidic acids, as well as their corresponding addition products with aniline, are described.

2. It was established that the reactivity of the oxide ring in the described glycidic acids is closely related to the steric hindrance factors created by the β-substituent. In the case of the branched-chain radicals a sharp drop is observed in the tendency of the oxide ring for addition reactions and an increase in its reactivity for exchange of the ester grouping by the anilido radical.

3. The transition from the ethyl ester of α-hydroxy-β-anilinocaproic acid to 2-propylindole was realized, and from the ethyl ester of α-hydroxy-β-anilinoisocaproic acid to 2-isopropylindole. At the same time a new method for the synthesis of 2-alkyl-substituted indoles was initiated.

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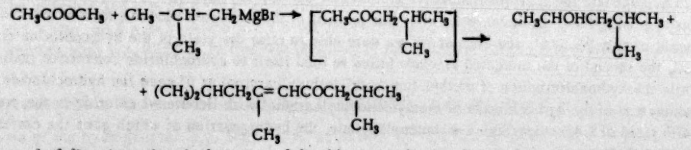
Leningrad State University

* T.p. = C. B. Translation pagination.

THE CONDENSATION OF ISOBUTENYLMAGNESIUM CHLORIDE WITH CARBONYL COMPOUNDS AND WITH TERTIARY HALIDES

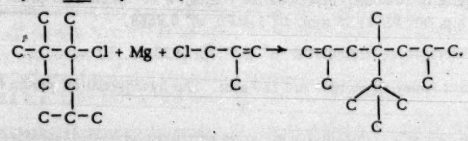
A. D. Petrov, V. L. Sushchinsky and L. D. Konovalchikov

The condensation of isobutylmagnesium halides with ketones (especially branched-chain) and with esters of monobasic and dibasic acids cannot be run by the normal schemes and used for the synthesis (through the corresponding tertiary alcohols and ditertiary glycols) of branched-chain aliphatic hydrocarbons. Thus, even methyl acetate reacts with this Grignard reagent, not with the formation of the tertiary alcohol, but by the scheme [1]:

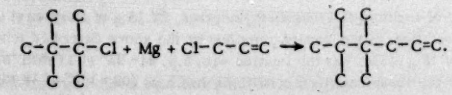


Instead of ditertiary glycols the esters of the dibasic acids give disecondary glycols [2], while pinacolin, as was shown in the present study, gives the pinacolin alcohol and the dehydrated pinacolin condensation product.

Taking into consideration the fact that the allyl halides react by the normal scheme with both acid esters (even such acids as oxalic [3]) and with pinacolin [4], we decided to investigate the reaction of methallyl chloride (isobutenyl chloride) with these carbonyl compounds, calculating on normal reaction schemes. Our expectations were justified, not only methyl acetate, but also the ester of isobutyric acid, gave the corresponding tertiary alcohols in high yields. In like manner the esters of succinic and adipic acids gave the ditertiary glycols: 1,1,4,4-tetraisobutenylbutanediol and 1,1,6,6-tetraisobutenylhexanediol. A tertiary alcohol was also obtained from pinacolin. In contrast to methyl-tert-butylallylcarbinol [4] we were unable to replace the hydroxyl group by chlorine in methyl-tert-butylisobutenylcarbinol, since here the HCl added at the tertiary bond of the isobutenyl radical. The alcohol was first hydrogenated, after which it readily formed the hydrochloride of methyl-tert-butylisobutylcarbinol. The condensation of this chloride with isobutenyl chloride in the presence of Mg gave 2,4,6-trimethyl-4-tert-butyl-1-heptene in 36% yield (after the reaction products had stood for two weeks.



It is interesting to mention that the condensation of a halide with two tertiary carbons, but of symmetrical structure, with allyl chloride, under the same conditions, led to only a 4.5% yield of 4,4,5,5-tetramethyl-1-hexene [5].

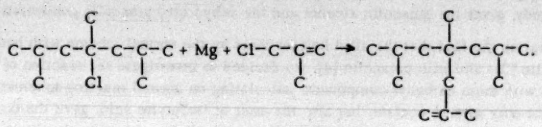


To determine the reason for the high yield of the hydrocarbon with two tertiary carbons (36%), whether it was due to the introduction of the methallyl radical or whether it was due to the asymmetrical character of the halide with the two tertiary carbons, we ran three condensation reactions: 1) 2,2,3,3-tetramethyl-3-chloropropane with methylallyl chloride, 2) 2,2,3,5-tetramethyl-3-chlorohexane with allyl chloride, and 3) 2,2,3-trimethyl-3-chlorohexane with methallyl chloride.

In the first case we obtained 2,2,3,3,5-pentamethyl-5-hexene in 6.5% yield, in the second case — 2,4-dimethyl-4-tert-butyl-6-heptene in 28% yield, and in the third case — 2,4-dimethyl-4-tert-butyl-1-heptene in 20% yield. As a result, it was established that the increased yields of hydrocarbons in the condensation reactions of halides of the allyl type with tertiary halides, containing two tertiary carbons in a row, can be accomplished by imparting to the latter an asymmetrical structure. (The indicated yields were obtained by allowing the reaction products to stand for a week).

Hydrogenation of the obtained tertiary diolefin alcohols and tetraolefin ditertiary glycols to the saturated alcohols and glycols, with their subsequent dehydration and hydrogenation, gave 2,4,6-trimethylheptane (obtained earlier [6] by the action of isobutylmagnesium bromide on methyl isobutyl ketone, and also by the action of the same reagent on mesityl oxide [7]), 2,6-dimethyl-4-isopropylheptane, 2,9-dimethyl-4,7-diisobutyldecane and 2,11-dimethyl-4,9-diisobutyldodecane. The second of these hydrocarbons was also recently obtained [8], but by a different method — through the acetylene glycol, which was synthesized from diisobutyl ketone and the Iotsich reagent.

For the same reason as in the case of the tertiary alcohol from isobutenylmagnesium chloride and pinacolin, we had to hydrogenate the methyldiisobutenylcarbinol and the isopropyldiisobutenylcarbinol before we could prepare their hydrochlorides. However, even after this the first of the indicated alcohols formed the hydrochloride in a total yield of only 3% at 0°, and even at 70° we were able to raise the yield of the hydrochloride only up to 10%. In general, the second of the indicated alcohols failed to lend itself to hydrochloride conversion under all conditions, while the hydrochlorination of methyl-tert-butyl-isobutylcarbinol at 0° gave the hydrochloride in 70% yield. The condensation of the hydrochloride of methyldiisobutylcarbinol with isobutenyl chloride in the presence of Mg gave a 42% yield of 2,4,6-trimethyl-4-isobutenylheptane, the hydrogenation of which gave the corresponding saturated hydrocarbon.



EXPERIMENTAL

2,4,6-Trimethyl-isobutylheptane. For reaction was taken 73 g of Mg, 226.5 g of isobutenyl chloride and 74 g of methyl acetate. After reaction had been initiated as the result of adding a small amount of isobutenyl chloride to the magnesium under ether, the mixture of methyl acetate and isobutenyl chloride, dissolved in 1.5 liters of ether, was added to the magnesium in the course of 10 hours. Fractionation through a 20-theoretical plate column gave 98 g of the tertiary alcohol (63% yield); b.p. 90–91° at 15 mm, n_D^{20} 1.4580, d_4^{20} 0.8568.

(1) Found %: C 78.28; H 11.20. $C_{10}H_{18}O$. Calculated %: C 77.86; H 11.76.

The alcohol was hydrogenated over Raney Ni at 130° and 160 atm. The hydrogenation product had b.p. 86–87° at 25 mm, n_D^{20} 1.4322, d_4^{20} 0.8252.

(2) Found %: C 76.14; H 14.32. $C_{10}H_{22}O$. Calculated %: C 75.88; H 14.01.

The hydrochlorination at 70° gave 19.7 of the chloride with b.p. 72–73° at 13 mm, n_D^{20} 1.4355, d_4^{20} 0.8677.

(3) Found %: Cl 19.83. $C_{10}H_{21}Cl$. Calculated %: Cl 20.06.

For condensation was taken: 35.4 g of 4-chloro-2,4,6-trimethylheptane, 27.18 g of isobutenyl chloride and 8 g of Mg. The reaction was run under the conditions of the Yavorsky method by the above described scheme. The main reaction product, isolated in an amount of 16 g (42%), was the fraction with b.p. 94–95° at 11 mm, n_D^{20} 1.4490, d_4^{20} 0.8004. The hydrogenate, obtained under the above described conditions, had b.p. 108–109° at 18 mm, n_D^{20} 1.4352, d_4^{20} 0.7812, MR_D 66.21; calc. 66.85.

(4) Found %: C 85.08; H 15.17. $C_{14}H_{30}$. Calculated %: C 84.75; H 15.24.

2,4,6-Trimethyl-4-tert-butylheptane. For reaction was taken 73 g of Mg, 100.3 g of pinacolin and 135 g of isobutenyl chloride. The reaction was run by the Yavorsky method. There was obtained 142 g of 2,2,3,5-tetramethyl-4-hexenen-3-olwith b.p. 46° at 4 mm, n_D^{20} 1.4502, d_4^{20} 0.8514. Earlier this alcohol had been obtained by

Whitmore [9], but by a different method (by the reaction of mesityl oxide with tert-butylmagnesium chloride) and in considerably lower yields, who gave for it physical constants that were close to ours. The structure of the alcohol, as the result of double bond shift proving to be methyl-tert-butylisocrotylcarbinol, was shown by oxidation, in which connection acetone (through the 2,4-dinitrophenylhydrazone with m.p. 125°) and a crystalline hydroxy acid with m.p. 141° were identified, the latter having been described earlier by Petrov and Lavrishcheva [4] (the mixed melting point with the earlier synthesized acid failed to be depressed).

When the hydrochlorination was run with the passage of HCl at 0° the monochloride was obtained in a total yield of 0.5%, while the dichloride was obtained in a yield of 80%: n_D^{20} 1.4710, d_4^{20} 1.023.

(5) Found %: Cl 33.32. $C_{10}H_{20}Cl_2$. Calculated %: Cl 33.53.

The hydrogenate of the alcohol had the following constants: b.p. 84.6–84.8° at 25 mm, n_D^{20} 1.4368, d_4^{20} 0.8393.

(6) Found %: C 75.44; H 14.22. $C_{10}H_{22}O$. Calculated %: C 75.88; H 14.01.

The hydrochlorination of 2,2,3,5-tetramethyl-3-hexanol was run under the conditions of gaseous HCl passage at 0°. The chloride had b.p. 72.6-73.5° at 28 mm, n_D^{20} 1.4455, d_4^{20} 0.8778. Then for the Yavorsky condensation there was taken: 56.6 g of 3-chloro-2,2,3,5-tetramethylhexane, 90.55 g of isobutenyl chloride and 48.6 g of Mg. The fraction with b.p. 92.5° at 12 mm was obtained in an amount of 24 g (36% yield), n_D^{20} 1.4584, d_4^{20} 0.8163.

(1) Found %: C 85.56; H 14.42. $C_{14}H_{28}$. Calculated %: C 85.62; H 14.37.

Constants of the hydrogenate: b.p. 105.5–106° at 19 mm, n_D^{20} 1.4460, d_4^{20} 0.7995.

(2) Found %: C 85.00; H 15.03. $C_{14}H_{30}$. Calculated %: C 84.75; H 15.26.

2,2,3,3,5-Pentamethylhexane. 2,2,3,3-Tetramethyl-3-chloropropane was obtained by the method of [10]. For reaction there was taken 36 g of the indicated chloride with m.p. 129°, 13 g of Mg and 36.2 g of methallyl chloride. There was isolated 2.8 g of fraction with b.p. 45–47° at 8 mm, n_D^{20} 1.4380, d_4^{20} 0.7743, MR_D 52.31; calc. 52.53. After hydrogenation there was obtained 2,2,3,3,5-pentamethylhexane, n_D^{20} 1.4260, d_4^{20} 0.7621, B. p. 172–173° at 755 mm. Literature [5]: n_D^{20} 1.4252, d_4^{20} 0.7615, b.p. 172–174° at 760 mm.

2,4-Dimethyl-4-tert-butylheptane. There was taken 94 g of 2,2,3,5-tetramethyl-3-chlorohexane, 61.22 g of allyl chloride and 24 g of Mg. The reaction products were fractionally distilled through a 20-theoretical plate column. There was obtained 27.2 g of fraction with b.p. 66–68° calc. 4 mm, (n_D^{20} 1.4521, d_4^{20} 0.8034, MR_D 61.70; calc. 61.23). The obtained olefin after hydrogenation had the following constants: 139–140° at 130 mm, n_D^{20} 1.4416, d_4^{20} 0.7964. This previously unknown hydrocarbon was also obtained by us by another method. 2,2,3-Trimethyl-5-hexene – 3-ol [5] was hydrogenated to 2,2,3-trimethyl-3-hexanol, which had the following constants: n_D^{20} 1.4370, d_4^{20} 0.8463, b.p. 87° at 55 mm. This alcohol was hydrochlorinated with HCl at 0°. The chloride had the following constants: n_D^{20} 1.4465, d_4^{20} 0.9010. The condensation of this chloride with isobutenyl chloride gave the olefin in 20% yield and with the following constants: b.p. 72–73° at 6 mm, n_D^{20} 1.4528, d_4^{20} 0.8055. The hydrogenate had b.p. 129–130° at 106 mm, n_D^{20} 1.4422, d_4^{20} 0.7964.

2,6-Dimethyl-4-isopropylheptane. For reaction was taken 102 g of methyl isobutyrate, 226 g of isobutenyl chloride and 7.3 g of Mg. The yield of fraction with b.p. 99.5° at 18 mm was 102 g (56%), n_D^{20} 1.4637, d_4^{20} 0.8699.

(3) Found %: C 79.02; H 12.13. $C_{12}H_{22}O$. Calculated %: C 79.06; H 12.16.

The dehydration of the alcohol over iodine gave the triolefin (2,6-dimethyl-4-isopropylidene-1,6-heptadiene) with b.p. 42° at 3 mm, n_D^{20} 1.4768, d_4^{20} 0.8153.

(4) Found %: C 87.13; H 12.18. $C_{12}H_{20}$. Calculated %: C 87.72; H 12.27.

Its structure was shown by oxidation, which gave acetone and diacetylacetone with m.p. 48°, the latter giving the diphenylhydrazone with m.p. 141°.

(5) Found %: N 17.82. $C_{19}H_{22}ON_4$. Calculated %: N 17.38.

The hydrogenate of this triolefin had the following constants: b.p. 35–36° at 2 mm, n_D^{20} 1.4336, d_4^{20} 0.7709, f.p. - 102° (to a glass).

(6) Found %: C 83.96, H 15.14. $C_{12}H_{26}$. Calculated %: C 84.61; H 15.39.

Hydrogenation of the isopropyldiisobutenylcarbinol gave the saturated tertiary alcohol with the following constants: b.p. 78–78.7° at 4 mm, n_D^{20} 1.4547, d_4^{20} 0.8536.

Found %: C 77.92; H 13.95. $C_{12}H_{26}O$. Calculated %: C 77.34; H 14.06.

Attempts to hydrochlorinate this alcohol at temperatures from 0 to 60° invariably led only to its quantitative dehydration and the formation of the monoolefin 2,6-dimethyl-4-isopropylideneheptane with b.p. 40-42° at 2 mm, n_D^{20} 1.4465, d_4^{20} 0.7905.

2,11-Dimethyl-4,9-diisobutyldodecane. To 144 g of Mg under ether was added several milliliters of isobutenyl chloride. When reaction began, then with water cooling of the flask and good stirring, at a rate of 2-3 drops a second, was added a mixture of 450 g of isobutenyl chloride and 174 g of dimethyl adipate, diluted with an equal volume of ether. After all of the mixture had been added the reaction mixture was heated another 24 hours on the water bath. The yield of 1,1,6,6-tetraisobutenylhexanediol with b.p. 160-165° at 3 mm was 277 g (81%), n_D^{20} 1.4950, d_4^{20} 0.9302.

Found %: C 79.41; H 11.52. $C_{22}H_{38}O_2$. Calculated %: C 79.04; H 11.38

A solution of 270 g of the glycol in 200 ml of methyl alcohol was hydrogenated. The hydrogenate of composition $C_{22}H_{46}O_2$ had the following constants: b.p. 155–160° at 3 mm; n_D^{20} 1.4410, d_4^{20} 0.8471. The saturated glycol (150 g) was dehydrated by boiling for 48 hours with 350 g of acetic anhydride and 160 g of sodium acetate at 140°. The yield of diolefin of composition $C_{22}H_{42}$ was 118 g, n_D^{20} 1.4522, d_4^{20} 0.8266. We were able to hydrogenate this diolefin to the saturated hydrocarbon only under the relatively drastic conditions of 130 atm., 300°, and a reaction time of 24 hours. B. p. 138–139° at 2 mm, n_D^{20} 1.4465, d_4^{20} 0.80379, f. p. −52°.

Found %: C 85.01; H 15.02. $C_{22}H_{46}$. Calculated %: C 85.07; H 14.93.

By oxidizing the diolefin it was shown to have the structure: 2,11-dimethyl-4,9-diisobutyl-3,9-dodecadiene. The amide with m.p. 122° was isolated. From the literature [11] the amide of isobutyric acid has m.p. 122°. In addition, the 2,4-dinitrophenylhydrazone with m.p. 122-123° was obtained, from the analysis data corresponding to the diketone of composition $C_{14}H_{26}O_2$.

Found %: C 51.98; H 5.722. $C_{26}H_{34}O_8N_8$. Calculated %: C 53.23; H 5.84.

It is interesting to mention that in the case of the tetraisobutylhexanediol, the same as for the isopropyldiisobutylcarbinol, we were unable to replace the hydroxyl groups by chlorine under the conditions of HCl passage at temperatures ranging from 0 to 60°.

2,9-Dimethyl-4,7-diisobutyldecane. The synthesis of 1,1,4,4-tetraisobutenylbutanediol from dimethyl succinate and isobutenyl chloride in the presence of Mg was run under the same conditions as described above. After distilling off the ether and diisobutenyl the resulting unsaturated glycol, without its isolation of fractionation, was hydrogenated over Raney Ni in an autoclave at 280°. The saturated glycol was dehydrated over $ZnCl_2$ by the method [12]. The resulting diolefin was hydrogenated in an autoclave over Raney Ni at an initial hydrogen pressure of 100 atm., at 280-320°, for 20 hours. The hydrogenate had the following constants: b.p. 115–118° at 2 mm, n_D^{20} 1.4436, d_4^{20} 0.7921, f.p. −59°.

Found %: C 84.63; H 15.22. $C_{20}H_{42}$. Calculated %: C 85.1; H 14.99.

SUMMARY

1. It was shown that isobutenylmagnesium chloride, in contrast to isobutylmagnesium chloride, reacts with pinacolin, methyl acetate, methyl isobutyrate and the esters of succinic and adipic acids by the normal scheme, with the formation of tertiary alcohols and ditertiary glycols.

2. From the synthesized tertiary alcohols and ditertiary glycols – by their hydrogenation, dehydration and subsequent hydrogenation of the olefinic and diolefinic hydrocarbons, and also by the condensation of saturated tertiary halides, with one and two tertiary carbon atoms, with isobutenylmagnesium chloride – there were synthesized for the first time: 2,4,6-trimethyl-4-isobutylheptane, 2,4,6-trimethyl-4-tert-butylheptane, 2,6-dimethyl-4-isopropylheptane, 2,11-dimethyl-4,9-diisobutyl-dodecane, and other branched-chain paraffin hydrocarbons.

3. It was shown that in the condensation of allyl-type halides with tertiary halides, having two tertiary carbon atoms in a row, in the presence of Mg (Yavorsky reaction), that the yields increase in the asymmetry of the halides.

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* See Consultants Bureau English translation, page 631.

REACTIVITY OF THE CARBONYL GROUP IN β-FURANIDONE

(TETRAHYDRO-3-FURANONE)

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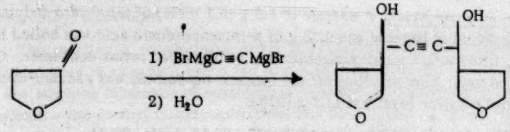
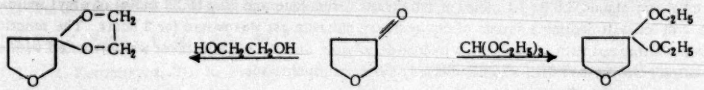
In our previous studies it was established that β-furanidone (tetrahydro-3-furanone) enters into all of the reactions characteristic for carbonyl compounds [1-3]; for example, when reacted with RMgX or ArMgX the tertiary alcohols are formed, from which the respective β-alkyl- and β-arylfuranidines (3-alkyl- and 3-aryltetrahydro-3-furanols) were then obtained. Tetrahydro-3-furanone exists only in its keto form, it fails to show reaction for its tautomeric form - dihydro-3-furanol (absence of color with ferric chloride).

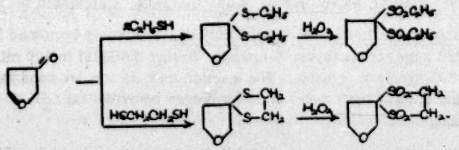
In the present study it was shown that tetrahydro-3-furanone also reacts with the Iotsich complex, forming bis[3-(3-hydroxytetrahydro)furyl]acetylene:



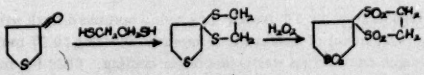
The reaction of tetrahydro-3-furanone with ethyl orthoformate (in the presence of mineral acid traces) [4] and with ethylene glycol (in the presence of p-toluenesulfonic acid) [5] gave, respectively, the diethyl ketal of tetrahydro-3-furanone (54% yield)and the ethylene ketal of tetrahydro-3-furanone (90% yield):



The reaction of tetrahydro-3-furanone proceeded in similar manner with ethyl mercaptan and with ethanedithiol, where the diethyl thioketal of tetrahydro-3-furanone (45% yield) and the ethylene thioketal of tetrahydro-3-furanone (54% yield) were respectively obtained, the oxidation of which with hydrogen peroxide gave the corresponding disulfones:



The sulfur analog of tetrahydro-3-furanone, β-thiophanone (3-thiophanone), when reacted with ethanedithiol gave the ethylene thioketal of 3-thiophanone in 76% yield, the oxidation of which with hydrogen peroxide gave the trisulfone:



EXPERIMENTAL

Bis[3-(3-hydroxytetrahydro)furyl]acetylene. To an ether solution of the Iotsich complex (7.2 g (0.3 mole) of magnesium, 32.7 g (0.3 mole) of ethyl bromide, 250 ml of absolute ether, and acetylene in a round-bottomed flask, fitted with reflux condenser, dropping funnel and mechanical stirrer, with ice cooling and stirring was added 25.8 g (0.3 mole) of tetrahydro-3-furanone in an equal volume of ether. The next day the reaction mixture was decomposed with hydrochloric acid. The ether layer was separated and the water layer was extracted in the extractor for 40 hours with ether. The combined ether extracts were dried and after distilling off the ether the residue was fractionated in

vacuo under nitrogen, where the following fractions were collected: 10 g of unchanged tetrahydro-3-furanone (40% of the amount taken for reaction; b.p. 58–60° (50 mm), n_D^{20} 1.4395) and 5.1 g of bis[3-(3-hydroxytetrahydro)furyl]acetylene, which distilled at 196–199° (3 mm) and crystallized in the receiver; m.p. 109.5–110.5° (from acetone).

Found %: C 60.85, 60.78; H 7.13, 7.44. $C_{10}H_{14}O_4$. Calculated %: C 60.60; H 7.12.

Bis[3-(3-hydroxytetrahydro)furyl]acetylene is readily soluble in water, alcohol, benzene, chloroform, carbon tetrachloride, dichloroethane, dioxane and tetrahydrofuranol. Its yield was 17%, based on taken, and 28%, based on reacted tetrahydro-3-furanone.

Tetrahydro-3-furanone Diethyl Ketal. To a mixture of 5.5 g (0.064 mole) of tetrahydro-3-furanone and 9.5 g (0.064 mole) of ethyl orthoformate (b.p. 143-144°) was added a drop of concentrated sulfuric acid, where slight heating of the reaction mixture was observed; after 1 hour the acid was neutralized with several drops of an alcoholic sodium ethylate solution.

Removal of the ethyl formate by distillation (b.p. 55-57°) and a 2-fold fractionation of the residue in vacuo gave 5.5 g (54%) of tetrahydro-3-furanone diethyl ketal:

B.p. 87–88° (30 mm), n_D^{20} 1.4279, d_4^{20} 0.9930, MR_D 41.50; calc. 41.87.
Found %: C 59.53, 59.58; H 9.84, 9.76. $C_8H_{16}O_3$. Calculated %: C 59.97; H 10.07.

Tetrahydro-3-furanone Ethylene Ketal. A mixture of 8.6 g (0.1 mole) of tetrahydro-3-furanone, 7 g (0.113 mole) of ethylene glycol, 50 ml of benzene and 0.12 g of p-toluenesulfonic acid was boiled for 8 hours in a 100 ml round-bottomed flask, fitted with a water-separation trap and attached reflux condenser. Calcium chloride was placed in the ice-cooled trap. After distilling off the benzene the residue was vacuum-distilled twice; the yield of tetrahydro-3-furanone ethylene ketal was 11.7 g (90%):

B.p. 79–79.5° (24 mm), n_D^{20} 1.4501, d_4^{20} 1.1465, MR_D 30.51; calc. 30.44.
Found %: C 55.05, 54.92; H 8.01, 7.96. $C_6H_{10}O_3$. Calculated %: C 55.36; H 7.75.

Tetrahydro-3-furanone Diethyl Thioketal. In a round-bottomed flask, fitted with reflux condenser and inlet tube, was placed 8.6 g (0.1 mole) of tetrahydro-3-furanone and 20 g (0.32 mole) of ethyl mercaptan, after which with ice-salt cooling a stream of dry hydrogen chloride gas was passed for 3 hours. The reaction mixture was then neutralized with diiute sodium hydroxide solution and the organic layer was extracted with ehter; the ether extract was washed with water and dried over calcium chloride.

After distilling off the ether the residue was fractionated twice in vacuo under a nitrogen stream; the yield of tetrahydro-3-furanone diethyl thioketal was 8.6 g (45%):

B.p. 93–93.5° (2 mm), n_D^{20} 1.5230, d_4^{20} 1.0806, MR_D 54.36; calc. 54.73.
Found %: C 50.17, 50.10; H 8.27, 8.38. $C_8H_{16}OS_2$. Calculated %: C 49.96; H 8.39.

Tetrahydro-3-furanone Diethyl Thioketal Disulfone. In a round-bottomed flask with reflux condenser was placed 3.6 g (0.0185 mole) of tetrahydro-3-furanone diethyl thioketal in 100 ml of glacial acetic acid and 4.2 g (0.037 mole) of 30% hydrogen peroxide. The reaction mixture was let stand for 2 hours at room temperature, after which another 5.3 g (0.0463 mole) of 30% hydrogen peroxide was added; further oxidation was pursued with boiling for 1.5 hours.

Removal of the acetic acid by vacuum-distillation gave as residue 3.8 g (80%) of tetrahydro-3-furanone diethyl thioketal disulfone; m.p. 109.5-110° (from acetic acid).

Found %: C 37.58, 37.86; H 6.28, 6.25. $C_8H_{16}O_5S_2$. Calculated %: C 37.48; H 6.29.

Tetrahydro-3-furanone Ethylene Thioketal. In a round bottomed flask with reflux condenser and gas inlet tube was placed 12 g (0.14 mole) of tetrahydro-3-furanone and 16 g (0.17 mole) of 1,2-ethanedithiol, after which a stream of dry hydrogen chloride gas was passed under cooling. Then the reaction mixture was neutralized with dilute sodium hydroxide solution and the organic layer was extracted with ether; the ether extract was washed with water and dired over calcium chloride. After distilling off the ether the residue was vacuum-distilled twice under a nitrogen stream; the yield of tetrahydro-3-furanone ethylene thioketal was 12.4 g (54%):

B.p. 98–98.5° (3 mm), n_D^{20} 1.5756, d_4^{20} 1.2629, MR_D 42.50; calc. 43.29.
Found %: C 44.56, 44.61; H 6.31, 6.38. $C_6H_{10}OS_2$. Calculated %: C 44.41; H 6.21.

Tetrahydro-3-furanone Ethylene Thioketal Disulfone. Three grams (0.0185 mole) of tetrahydro-3-furanone ethylene thioketal was oxidized with 9.5 g (0.083 mole) of 30% hydrogen peroxide, as described above. The yield of tetrahydro-3-furanone ethylene thioketal disulfone was 4.1 g (98%): m.p. 154.5-155° (from acetic acid).

Found %: C 31.78, 32.11; H 4.45, 4.56. $C_6H_{10}O_5S_2$. Calculated %: C 31.84; H 4.46.

3-Thiophanone Ethylene Thioketal. From 6.5 g (0.064 mole) of 3-thiophanone and 6.4 (0.068 mole) of 1,2-ethanedithial, by the method described for the preparation of tetrahydro-3-furanone ethylene thioketal, was obtained 8.6 g (76%) of 3-thiophanone ethylene thioketal:

B.p. 128–128.5° (4 mm), n_D^{20} 1.6317, d_4^{20} 1.3040, MR_D 48.76; calc. 49.53.
Found %: C 40.25, 40.12; H 5.66, 5.65. $C_6H_{10}S_3$. Calculated %: C 40.41; H 5.74.

3-Thiophanone Ethylene Thioketal Trisulfone. The 3-thiophanone ethylene thioketal (4.4 g) (0.025 mole) was oxidized with 19 g (0.167 mole) of hydrogen peroxide, as described above. The yield of 3-thiophanone ethylene thioketal trisulfone was 6.4 g (95%): m.p. 210° (with decompn.), from acetic acid.

Found %: C 26.61, 26.70; H 3.75, 3.85. $C_6H_{10}O_6S_3$. Calculated %: C 26.29; H 3.68.

SUMMARY

1. The reaction of tetrahydro-3-furanone with the Iotsich complex leads to the formation of bis[3-(3-hydroxytetrahydro)furyl]acetylene.

2. The reaction of tetrahydro-3-furanone with ethyl orthoformate, ethylene glycol, ethyl mercaptan and ethanedithiol gave in excellent yields the new diethyl and ethylene ketals of tetrahydro-3-furanone and the new diethyl and ethylene thioketals of tetrahydro-3-furanone. Oxidation of the tetrahydro-3-furanone thioketals gave the disulfones – the diethyl thioketal disulfone and the ethylene thioketal disulfone. 3-Thiophanone ethylene thioketal and its oxidation product, the corresponding trisulfone, were also obtained.

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Moscow State University

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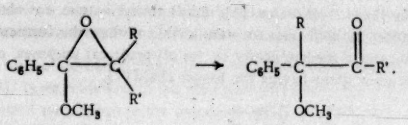
CYCLIC ACETALS OF HYDROXYCARBONYL COMPOUNDS

VI. ISOMERIZATION OF THE METHYL LACTOLIDES OF α-KETO ALCOHOLS INTO THE METHYL ETHERS OF THE ISOMERIC α-KETO ALCOHOLS

T. I. Temnilova, A. K. Petryaeva and S. S. Skorokhodov

In the previous studies of this series it was shown that the methyl lactolides of α-keto alcohols can suffer various transformations under the influence of acidic agents: hydrolysis to the keto alcohols [1, 2], dimerization to the corresponding substituted dioxanes [1, 2], formation of ethers of α-keto alcohols [2, 3], or isomerization with the formation of methyl ethers of the isomeric α-keto alcohols [2, 3]. The purpose of the present study was to seek a catalyst, assuring reaction to proceed only in one direction, namely, in the direction of transforming the methyl lactolide of the keto alcohol into the methyl ether of its isomeric keto alcohol:



(I) (II)

Having found a catalyst, directing the process in such manner that the oxide ring is opened only in one place, it became possible to make a comparison of the conditions necessary for the isomerization of methyl lactolides of secondary α-keto alcohols, where hydrogen shifting (R=H) is observed, with the conditions for the isomerization of methyl lactolides of tertiary α-keto alcohols, where the hydrocarbon group shifts; and, finally, it was of interest to determine if in the isomerization of compounds, containing different hydrocarbon groups, only one of these groups would predominantly shift, as is observed for the pinacolin and other rearrangements.

The methyl lactolides of the following α-keto alcohols were studied: ethylbenzoylcarbinol [(I) R=H, R'=C_2H_5], dimethylbenzoylcarbinol [(I) R=R'=CH_3], methylethylbenzoylcarbinol [(I) R=C_2H_5, R'=CH_3] and methyl-n-butylbenzoylcarbinol [(I) R=C_4H_9, R'=CH_3]. The methyl lactolides of the first two keto alcohols were obtained and characterized earlier [2]; the methyl lactolides of the keto alcohols, containing different hydrocarbon groups, were obtained for the first time in the present work by the earlier developed method, proceeding from the corresponding bromo ketones. When hydrolyzed the methyl lactolides give α-keto alcohols, identical with the α-keto alcohols obtained in the hydrolysis of the bromo ketones, serving as the starting substances for the preparation of the methyl lactolides.

The isomeric transformations of a number of methyl lactolides were realized in previous studies. As isomerization agents for the methyl lactolide of methylbenzoylcarbinol [(I) R= H; R'=CH_3] were used oxalic and dichloroacetic acids in benzene solution [3]; an attempt to use oxalic acid for the isomerization of the methyl lactolide of dimethylbenzoylcarbinol (R=R'=CH_3) proved unsuccessful; only the oxalate of dimethylbenzoylcarbinol was isolated [2]. Isomerization by means of magnesium bromide etherate in ether solution also failed to give satisfactory results, since here the isomerization product was obtained only in small yield [2]. The etherate of magnesium bromide in boiling diethyl ether was also used by Stevens [4, 5] for the isomerization of the methyl lactolides of α-keto alcohols.

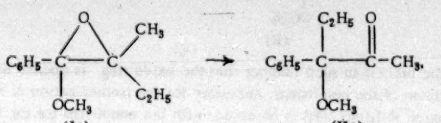
In the present work we investigated the isomerizing influence of other compounds, containing magnesium, on the methyl lactolide of ethylbenzoylcarbinol [(I) R=H, R'=C_2H_5], and namely, methylmagnesium bromide in ether and methylmagnesium chloride in ether; in both cases the isomerization product is obtained only in minute amount.

It appeared of interest to study the action of boron trifluoride on the methyl lactolides of the alkylaryl α-keto alcohols. It was found that the etherate of boron trifluoride exerts a different influence on the methyl lactolide of the secondary keto alcohol, ethylbenzoylcarbinol, than it does on the methyl lactolides of the tertiary keto alcohols. In the first case only dimerization is observed with the formation of 2,5-dimethoxy-3,6-diethyl-2,5-diphenyl-1,

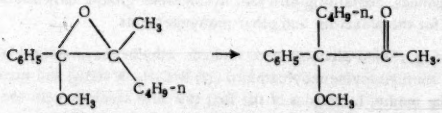
4-dioxane. The treatment of the methyl lactolides of dimethylbenzoylcarbinol and methylethylbenzoylcarbinol with the etherate of boron trifluoride results in partial isomerization, but in the first case, together with the methoxy ketone (confirmed by its infrared spectrum), a considerable amount of the anhydro dimer is formed; the structure of this dimer, described by A. E. Favorsky and N. Mandryko, remains obscure [6, 2].

Zinc chloride proved to be a very good catalyst for the isomerization of the methyl lactolides; the methyl lactolide of ethylbenzoylcarbinol was isomerized by two methods: by the action of $ZnCl_2$ in ether solution, and by heating the methyl lactolide to 60-70° with pieces of porous plate, impregnated with zinc chloride, with subsequent distillation from the pieces. In both cases a completely homogeneous product was obtained, distilling within 0.5° and being the methyl ether of the keto alcohol [(II) R=H, R'=C_2H_5]. Isomerization fails to proceed when the methyl lactolide is distilled from pieces of porous plate without the $ZnCl_2$; isomerization is also absent under the influence of pieces of porous plate with $ZnCl_2$ in the cold.

More drastic conditions are required for the isomerization of the methyl lactolides of the tertiary α-keto alcohols; we were able to realize their isomerization only by the addition of several milliliters of a saturated ether solution of $ZnCl_2$ to the methyl lactolide, with subsequent heating of the solution at about 110° for 1 hour. The methyl ether of methylphenylacetylcarbinol was described earlier [2]. A completely homogeneous reaction product was obtained in the isomerization of the methyl lactolide of methylethylbenzoylcarbinol (III), and also of the methyl lactolide of methyl-n-butylbenzoylcarbinol (IV). The structure of the isomerization products was established by the method of Beckmann rearrangement (Order II) of their oximes [5]. Ethyl phenyl ketone was obtained in the first case, in the second, -n-butyl phenyl ketone; in both cases we were unable to show the formation of acetophenone. From these data it follows that the rearrangement predominantly or, for all practical purposes, completely proceeds with the migration (shifting) of the hydrocarbon group having the longer chain [7].



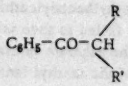
(Ia) (IIa)



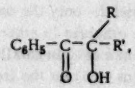
(Ib) (IIb)

A similar study was made by Stevens and Dykstra, who studied the rearrangement of the methyl lactolide of methylethyl-p-phenylbenzoylcarbinol under the influence of $MgBr_2$; they also found the process to proceed only in one direction with migration of the ethyl group [5].

Having gained a certain collection of methyl lactolide speciments (I) and their genetically associated compounds – the ketones (III) and the α-keto alcohols (IV), in structure corresponding to the studied α-methyl lactolides and the methyl ethers of the isomeric α-keto alcohols (II)



(III)



(IV)

we approached the study of their infrared absorption spectra for the purpose of developing a method for directly proving the presence of the α-oxide ring in methyl lactolides.

In principle an answer to this problem possesses great significance, since up to now the conclusion that an oxide ring is present in α-methyl lactolides has been based on indirect evidence, namely, on the basis of their great reactivity: their ease of transformation into α-keto alcohols when hydrolyzed, or when reacted with different reagents; the ease with which they are transformed into the corresponding α-keto alcohol derivatives.

In studying the methyl lactolides of the α-keto alcohols, and also the substances formed from them under various transformations, it was found that successful use of their ultraviolet absorption spectra could be made. The ultraviolet absorption spectra made it possible to establish the absence of the carbonyl group in the compounds that are formed in the reaction of α-halo ketones with sodium methylate, and thus gave assurance that the methyl ether of the keto alcohol is not formed in the reaction. Spectral study of the transformation products of the methyl lactolides of the α-keto alcohols confirms the formation here of compounds that contain the carbonyl group, being either in conjugation or not in conjugation with the aromatic nucleus [2, 3]. The direct determination of the oxide grouping in the methyl lactolides of the α-keto alcohols by the method of studying their ultraviolet absorption spectra is made essentially difficult for the reason that, apparently, the absorption maximum of a three-membered oxide ring is found at about 210 mμ [8, 9], i.e. outside of the transparent limits for the solvents used [10]. This circumstance should also be much circumspect with respect to the above presented data, obtained in the work with alcohol solutions.

The study of the infrared spectra of compounds, containing the α-methoxy oxide ring, was made on the methyl lactolides of: dimethylbenzoylcarbinol [(I) R=R'=CH_3], methylethylbenzoylcarbinol [(I) R=CH_3, R=C_2H_5] and methyl-n-butylbenzoylcarbinol [(I) R'=CH_3, R=n-C_4H_9].

The presence of the CH_3O group in the methyl lactolides of the α-keto alcohols excluded the possibility of using the frequency, characteristic for the C-O bond, for characterizing the oxide ring. Here it appeared necessary to determine the frequencies that correspond to the deformations suffered by the oxide ring. Taking into consideration the strain present in a three-membered oxide ring (in ethylene oxide the COC angle =65°6'), it could be expected that the difference between the C-O-C frequencies in the open chain and in the ring will be considerable.

The simplest molecule, containing a three-membered oxide ring, is ethylene oxide. In the studies of Bonner [11] and Linnett [12], later reviewed in the monograph by Herzberg [13], it was shown that the basic frequencies of 1267, 863 and 808 cm^{-1} correspond to the deformations of the oxide ring. These frequencies are also active in the spectra of combined light scattering (Raman spectra) [14].

As regards the frequencies, corresponding to the ether bond C-O-C, in the majority of cases they lie in the region of 1100-1300 cm^{-1} [15, 16]. Proceeding from these data, we did not try to determine the 1267 cm^{-1} frequency, since it would have been difficult to identify. The 808 cm^{-1} is extremely weak [11, 12] and consequently it also was excluded from our consideration.

The voluminous literature data on the infrared spectra of ethylene oxide homologs fail to give a united representation as to the characteristic frequencies: thus, in the short report of Field and co-authors only the frequency in the limits of 1240-1260 cm^{-1} is considered to be characteristic [17] (the spectra are not given). Shreve and coworkers, in comparing the spectra of monosubstituted aliphatic oxides with those of the corresponding hydrocarbons (decane, dodecane and tetradecane), arrive at two characteristic absorption maxima at 10.9 mμ (917 cm^{-1}) and 11.9 mμ (840 cm^{-1}) [18]. Patterson, on the basis of the spectra for 26 compounds, containing the three-membered oxide ring, considers the frequencies around 1260 cm^{-1} to be characteristic, and also mentions two frequencies in the 10-13 mμ (1000-769 cm^{-1}) region. In connection with our studies it is interesting to mention that the spectra presented by him for some of the glycidyl ethers show an absorption maximum around 920 cm^{-1} [19]. The combined light scattering spectra (Raman spectra) data speak in favor of the frequencies at ~ 910 and ~ 1260 cm^{-1} [20].

Taking into consideration all of these facts and the orientating spectrographic study made by us of all of the specimens in the 2000-768 cm^{-1} region, and also in the 3500-3000 cm^{-1} region, we measured the absorption spectra of the methyl lactolides and their genetically associated compounds in the 830-925 cm^{-1} region, and also in the absorption region of the carbonyl group within the limits of 1470-1750 cm^{-1}. The work was done with a Hilger infrared spectrometer, using a thin layer of material (50 and 150 μ) and a NaCl prism. From the presented absorption curves * it can be seen that the methyl lactolides (Curves I in Figs. 1, 2 and 3) fail to show the intense absorption maximum that is characteristic for the carbonyl group. The slight maximum around 1690 cm^{-1}, corresponding to the conjugated carbonyl group, can be explained by the formation of benzoyl-containing impurities of the methyl ether of the keto alcohol; the presence of the keto alcohol itself as impurity is excluded by the analysis data and

* The same Roman numerals are used for numbering the absorption curves and the earlier presented formulas of the corresponding investigated compounds.

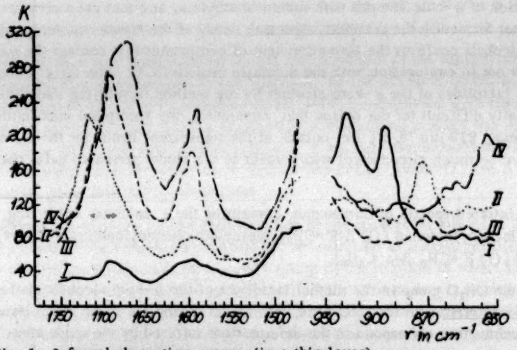


Fig. 1. Infrared absorption curves (in a thin layer).
I) -methyl lactolide of dimethylbenzoylcarbinol, II) methyl ether of methylphenylacetylcarbinol, III) isopropyl phenyl ketone, IV) -dimethylbenzoylcarbinol.

by the absence of the hydroxyl group, which was proved by spectral analysis. Consequently, the reaction between α-bromo ketones and sodium methylate, with direct replacement of the bromine by methoxyl proceeds insignificantly, which we were able to show only by the spectrometric method. The methyl ethers of the keto alcohols, obtained in the isomeric transformation of the methyl lactolides, contain an unconjugated carbonyl group, for which the frequencies are 1724, 1720 and 1721 cm^{-1} (Curves II in Figs. 1, 2 and 3). In contrast to them, the frequency of the carbonyl group for the ketones, possessing a benzoyl group, according to the literature [21], proves to be 1692, 1690 and 1689 cm^{-1} (Curves III in Figs. 1, 2 and 3); for the α-keto alcohols, containing a benzoyl group, this frequency is shifted even more due to the presence of the hydroxyl group (Curves IV in Figs. 1 and 3). The presented results are in complete agreement with the chemical study data. For all of the given Figures the maximum around 1600 cm^{-1} belongs to the phenyl nucleus.

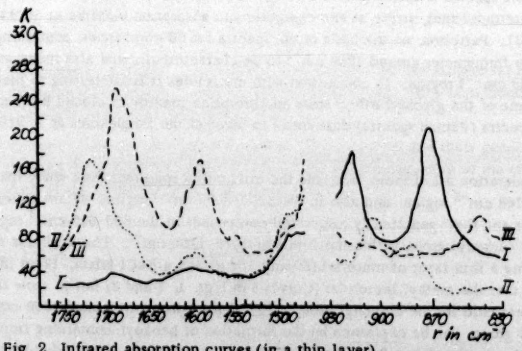


Fig. 2. Infrared absorption curves (in a thin layer).
1) methyl lactolide of methylethylbenzoylcarbinol, II) -methyl ether of ethylphenylacetylcarbinol, III) sec-butyl phenyl ketone.

When the absorption curves of the methyl lactolides (Curves I in Figs. 1, 2 and 3) in the 830-930 cm^{-1} region are examined it can be seen that they all possess an intense absorption maximum at 917 cm^{-1}, which maximum is absent on the curves of all of the other compounds and, which is especially important, is absent on the curves of the isomeric keto alcohol methyl ethers (Curves II).

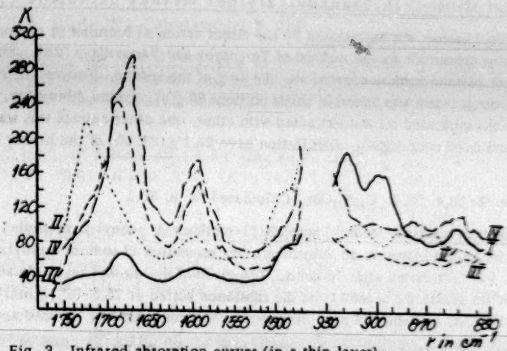
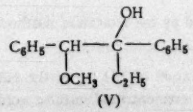


Fig. 3. Infrared absorption curves (in a thin layer). I) -methyl lactolide of methyl-n-butylbenzoylcarbinol, II) -methyl ether of n-butylphenylacetylcarbinol, III) 2-methyl-1 phenyl-1-cyclohexanone, IV) -methyl-n-butylbenzoylcarbinol.

The absorption curves for the methyl lactolides (Curves I in Figs. 1, 2 and 3) also have another intense frequency at 896, 874 and 899 cm^{-1}, respectively. The variation in the position of these frequencies for the methyl lactolides themselves and the presence of close maxima in the spectra of their isomeric compounds (Curves II in Figs. 1, 2 and 3) does not permit their clear interpretation. To us it seems possible to consider only the frequency of 917 cm^{-1} as being characteristic for the α-oxide grouping found in alkylaryl α-methyl lactolides. This consideration is supported by the fact that in our measured absorption spectrum for the methyl lactolide of n-propylbenzoylcarbinol [(I), R=C_3H_7, R'=H]* an intense frequency was found at 919 cm^{-1}, i.e. a change in the carbon skeleton failed to essentially change the position of the frequency of the methoxy oxide cycle.

Along with solving the basic problems, presented in this study, we made the transition from the methyl ether of ethylbenzoylcarbinol to the monomethyl ether of the glycol by treating the ether of the keto alcohol with phenylmagnesium bromide. From the literature it is known that the action of organomagnesium compounds on α-keto alcohols always results in the practically complete formation of only one of two possible stereoisomeric forms, in which connection, by combining the components in various manner it is possible to obtain one or the other stereoisomeric form at will [22].

On the basis of the data obtained by us it can be assumed that the same will also always be observed for the action of organomagnesium compounds on the methyl ethers of α-keto alcohols. The glycol monomethyl ether, ethylphenyl-α-methoxybenzylcarbinol (V), isolated as the result of this reaction, was completely homogeneous and had m.p. 83° (α-form)**



(V)

The β-form of the same compound, without the stereoisomer as impurity, is obtained by the action of ethylmagnesium bromide on the methyl ether of benzoin; the substance melts at 64°.

* Performed for us by V. A. Ivanova.

** The designation α and β is given in accord with the suggestion of Tiffeneau and Levy [22].

EXPERIMENTAL

I. Preparation of Methylethylbenzoylcarbinol Methyl Lactolide (Ia)*

a) sec-Butyl phenyl ketone was brominated by the direct action of bromine in carbon tetrachloride, and under the influence of dioxane dibromide by the method of Terentyev and Yanovskaya [23]. The yields were approximately the same, but the latter method is more convenient. To 20 g of the ketone, dissolved in 20 ml of dioxane, with constant cooling to room temperature was added in small portions 60 g of dioxane dibromide. The reaction mass was poured into water and the separated oil was extracted with ether; the ether extract was washed with water, then with thiosulfate solution, and dried over $MgSO_4$. Distillation gave 24.1 g (81.1%) of the bromo ketone, boiling at 111-113° (3 mm).

Found %: Br 33.4, 33.4. $C_{11}H_{13}OBr$. Calculated %: Br 33.1

b) Methylethylbenzoylcarbinol Methyl Lactolide (1-methoxy-1-phenyl-2-methyl-1-butene oxide) was obtained by adding 52.27 g of the bromo ketone to an anhydrous ether suspension of sodium methylate, prepared from 16 g of sodium. The reaction was terminated after 10 hours. The yield of the methyl lactolide with b.p. 101-102° (7 mm) was 24.9 g (63.6%). When distilled a second time the substance boiled at 75.5-76° (3 mm). Its ultraviolet spectrum has maxima at 265, 257, 254, 252 and 243 mμ. Its structure was confirmed by infrared analysis.

d_4^{14} 0.9993, n_a^{14} 1.4951, MR_a 56.04. $C_{12}H_{16}O_2$ F 3. calc. 55.15.
Found %: C 74.64, 74.89; H 8.18, 8.27; OCH_3 16.1. $C_{12}H_{16}O_2$. Calculated %: C 75.00; H 8.33; OCH_3 16.2.

II. Preparation of Methylethylbenzoylcarbinol

a) Hydrolysis of Methylethylbenzoylcarbinol Methyl Lactolide. The methyl lactolide (3.48 g) was heated with 30 ml of 5% H_2SO_4 on the boiling water bath for 4 hours. The cooled reaction product was extracted with ether, and the ether extract was dried over $MgSO_4$. Vacuum-distillation gave 1.9 g (58.9%) of methylethylbenzoylcarbinol with b.p. 115-115.5° at 6 mm. Its spectrum in the ultraviolet has maxima at 320 and 284 mμ, which testifies to the presence of the benzoyl group.

d_4^{19} 1.054, n_a^{19} 1.5210, MR_a 51.42. $C_{11}H_{14}O_2$ F 3. calc. 50.56.
Found %: C 73.93; H 7.73; active H 0.99, 0.98. $C_{11}H_{14}O_2$. Calculated %: C 74.16; H 7.86; active H 1.0.

b) Hydrolysis of α-Bromo-sec-butyl Phenyl Ketone. A mixture of 9.52 g of the bromo ketone and 1.67 g of NaOH in aqueous-alcohol solution (20 ml alcohol + 20 ml water) was heated on the boiling water bath for 2 hours. The cooled oil was extracted with ether and dried over $MgSO_4$. Vacuum-distillation at 113-113.5° (5 mm) gave 2.23 g of the keto alcohol as a clear yellowish liquid; n_a^{15} 1.5238.

Found %: C 73.84; H 8.14. $C_{11}H_{14}O_2$. Calculated %: C 74.16; H 7.86.

III. Preparation of Methyl-n-butylbenzoylcarbinol Methyl Lactolide (Ib)*

a) 2-Bromohexane. To 112 g of 2-hexanol at the boil was added 85 g of PBr_3 with vigorous stirring; the reaction was continued for 5 hours; after cooling the bromide was decanted from the phosphorus compounds, washed with water, and dried over $MgSO_4$. Fractional distillation through a column gave 95 g (52.2%) of the bromide with b.p. 47-48° at 20 mm. Literature: b.p. 144-146° [24].

b) 2-Methyl-1-phenyl-1-hexanol was obtained by the literature method [24], but with replacement of the 2-bromohexane. B.p. 130-132° at 5 mm.

c) 2-Methyl-1-phenyl-1-hexanone. To a mixture of 161.3 g of the carbinol and 83 g of $K_2Cr_2O_7$ in 484 ml of water was gradually added (at 30-40°) 62.5 ml of concentrated sulfuric acid that had been diluted with 120 ml of water. Then the mixture was heated for 1 hour to 70°, the ketone separated, and the aqueous solution extracted with ether. The ketone was steam-distilled. The yield of ketone was 117.3 g (82.3%). Its structure was confirmed by infrared analysis.

B.p. 109–110° at 3 mm, d_4^{20} 0.957, n_D^{20} 1.5070, MR_D 59.17. $C_{13}H_{18}O$ F 3. calc. 58.64.
Found %: C 81.76, 81.81; H 9.86, 9.94. $C_{13}H_{18}O$. Calculated %: C 82.06; H 9.54.

* Work done by S. S. Skorokhodov.

d) 2-Bromo-2-methyl-1-phenyl-1-hexanone. For reaction was taken 30 g of the ketone, 30 ml of dioxane and 43 g of dioxane dibromide (same conditions as above). The yield of the bromo ketone with b.p. 137-139° at 5 mm was 30.19 g (71%).

Found %: Br 30.0. $C_{13}H_{17}OBr$. Calculated %: Br 29.7.

e) Methyl-n-butylbenzoylcarbinol Methyl Lactolide. (1-methoxy-1-phenyl-2-methyl-1-hexene oxide). The synthesis was made from 17.1 g of the bromo ketone and the sodium methylate obtained from 6 g of Na. The reaction was terminated after 12 hours. The yield of the methyl lactolide was 8.2 g (58.3%). Its structure was confirmed by infrared analysis.

B.p. 97–98° (2 mm), d_4^{20} 0.9958, n_D^{20} 1.4884, MR_D 64.86. $C_{14}H_{20}O_2$ ∫ 3. calc. 64.47.
Found %: C 76.59, 76.63; H 9.20, 9.36; OCH_3 14.2. $C_{14}H_{20}O_2$. Calculated %: C 76.32; H 9.15; OCH_3 14.1.

IV. Preparation of Methyl-n-butylbenzoylcarbinol

a) Hydrolysis of 2-Bromo-2-methyl-1-phenyl-1-hexanone. (Same hydrolysis conditions as above). Starting with 6.46 g of the bromo ketone, the yield of the keto alcohol was 3.71 g (74.4%). Its structure was confirmed by infrared analysis.

B.p. 127–128° (4 mm), d_4^{20} 1.016, n_D^{20} 1.5150, MR_D 61.21. $C_{13}H_{18}O_2$ ∫ 3. calc. 60.17.
Found %: C 75.27, 75.47; H 8.91, 8.54. $C_{13}H_{18}O_2$. Calculated %: C 75.69; H 8.79.

b) Hydrolysis of Methyl-n-butylbenzoylcarbinol Methyl Lactolide. (Same conditions as above). Starting with 5.61 g of the methyl lactolide, the yield of the keto alcohol with b.p. 118-119° at 2 mm was 2.89 g. Its infrared spectrum was the same as that of the keto alcohol obtained from the bromo ketone.

d_4^{20} 1.021, n_D^{20} 1.5192, MR_D 60.94. $C_{13}H_{18}O_2$ ∫ 3. calc. 60.17.
Found act. H 1.01. Calculated act. H 1.0.

V. Isomerization of α-Keto Alcohol Methyl Lactolides Under the Influence of Zinc Chloride

1) Isomerization of Ethylbenzoylcarbinol Methyl Lactolide [(I) R=H, R'=C_2H_5].*

a) The methyl lactolide (9.5 g) (b.p. 94° at 10 mm) was heated for 30 minutes at 60-70° over pieces of porous plate, impregnated with $ZnCl_2$ solution and dried at 110°; the substance, vacuum-distilled from these pieces, distilled completely at 104-105° (7 mm).

b) To the methyl lactolide was gradually added 7 drops of an ether solution of $ZnCl_2$. Strong heating up with ether frothing was observed when the first drop was added, the reaction was much less violent with further addition of the drops and a white precipitate appeared, which vanished on shaking. After distilling off the ether a product was obtained that distilled completely at 99.5-99.8° (5 mm).

d_4^{20} 1.015, n_D^{20} 1.5050, MR_D 52.00. $C_{11}H_{14}O_2$ ∫ 3 calc. 51.05.

The semicarbazone of the phenylpropionylcarbinol methyl ether, recrystallized from ethyl alcohol, has m.p. 150-151°.

Found %: N 17.5. $C_{12}H_{17}O_2N_3$. Calculated %: N 17.8.

The 2,4-dinitrophenylhydrazone - yellow crystals; m.p. 140-141° (from ethyl alcohol).

Found %: CH_3O 8.5, 8.9; N 15.73, 15.90. $C_{17}H_{18}O_5N_4$. Calculated %: OCH_3 8.7; N 15.6.

2) Isomerization of Dimethylbenzoylcarbinol Methyl Lactolide [(I) R=R'=CH_3]** To 11.12 g of methyl lactolide was added 3 ml of a saturated solution of anhydrous $ZnCl_2$ in anhydrous ether. After heating the solution for 1 hour at 110° the substance was vacuum-distilled. The yield of methylphenylacetylcarbinol methyl ether, distilling at 89–90° (5 mm), n_D^{15} 1.5086, was 9.65 g (87%). The substance is identical with that obtained earlier in the isomerization of the same lactolide with $MgBr_2$. The structure of the methoxy ketone was confirmed by infrared analysis.

* Work done by A. K. Petryaeva.
** Work done by S. S. Skorokhodov.

3) Isomerization of Methylethylbenzoylcarbinol Methyl Lactolide (III).* To 8.53 g of the methyl lactolide was added 3.25 g of a saturated solution of anhydrous $ZnCl_2$ in anhydrous ether. After heating for 1 hour at 120° the substance was vacuum-distilled. The yield of the methyl ether of ethylphenylacetylcarbinol (3-methoxy-3-phenyl-2-pentanone) was 5.58 g. Its structure was confirmed by infrared analysis.

B.p. 98–99° (5 mm), d_4^{20} 1.025, n_D^{20} 1.5050, MR_D 55.56. $C_{12}H_{16}O_2$. calc. 55.85.
Found%: C 74.98, 74.58; H 8.51, 8.36; OCH_3 16.5. $C_{12}H_{16}O_2$. Calculated%: C 74.96; H 8.39; OCH_3 16.2.

Preparation of Ethylphenylacetylcarbinol Methyl Ether Oxime. To a solution of 2.4 g of hydroxylamine hydrochloride in 15 ml of water was added 10 ml of a 10% aqueous NaOH solution and then 1 g of the methoxy ketone and sufficient methyl alcohol to completely dissolve the methoxy ketone. The solution was heated on the boiling water bath for 10 minutes, then cooled with ice water and allowed to stand over night. The next day the white needlelike crystals with m.p. 97 - 98° were filtered. The crystals were washed with water and dried. The yield of oxime was 0.81 g (75%). After recrystallization from ethyl alcohol the crystals melted at 98-99°.

Found %: N 6.87. $C_{12}H_{17}O_2N$. Calculated %: N 6.76.

Rearrangement of the Oxime [5]. To 0.600 g of the oxime (0.003 mole) was added 15 ml of 10% aqueous NaOH and then 1.05 g (0.006 mole) of benzenesulfonyl chloride. The mixture was shaken until all of the oxime had gone into suspension. A slight heating up of several degrees was observed. Then another 0.54 g (0.003 mole) of benzenesulfonyl chloride was added. Shaking was continued to complete disappearance of the benzenesulfonyl chloride. The obtained oil was separated and steam-distilled. There was obtained 0.290 g (80.8%) of ketone. Its semicarbazone, recrystallized from ethyl alcohol, melted at 173-174° and failed to be depressed when mixed with authentic ethyl phenyl ketone semicarbazone.

4) Isomerization of Methyl-n-butylbenzoylcarbinol Methyl Lactolide. To 4.05 g of the methyl lactolide was added 1.5 ml of a saturated solution of anhydrous $ZnCl_2$ in anhydrous ether. After heating for 1 hour at 140-150° the substance was vacuum-distilled. The yield of methoxy ketone (3-methoxy-3-phenyl-2-heptanone) was 2.97 g (73.4%). Its infrared absorption spectrum shows the presence of a carbonyl group, not conjugated with the phenyl radical, and the absence of an oxide ring.

B.p. 108-109° (2 mm), d_4^{20} 0.992, n_D^{20} 1.5003, MR_D 65.29. $C_{14}H_{20}O_2$. Calculated 64.90.
Found %: C 76.45, 76.16; H 91.12, 9.30; OCH_3 13.9. $C_{14}H_{20}O_2$. Calculated %: C 76.32; H 9.15; OCH_3 14.1.

n-Butylphenylacetylcarbinol Methyl Ether Oxime was prepared in the same manner as the preceding specimen, starting from 2 g of the methoxy ketone; heating was maintained for 15 minutes. The white, petal-shaped crystals deposited only after 3 days of standing. The crystals were washed with water and dried. The yield of substance with m.p. 71-72° was 1.87 g (87.7%). The melting point was the same after recrystallization from ethyl alcohol.

Found %: N 5.94. $C_{12}H_{21}O_2N$. Calculated %: N 5.95.

Rearrangement of the Oxime. To 1.01 g of the oxime of the methoxy ketone (0.0045 mole) was added 22.5 ml of 10% aqueous NaOH and 1.58 g (0.009 mole) of benzenesulfonyl chloride. The mixture was shaken until the oxime went into suspension, after which another 0.81 g (0.0045 mole) of benzenesulfonyl chloride was added. Shaking was continued to complete disappearance of the benzene-sulfonyl chloride. The obtained oil was separated and steam-distilled, the yield of crude product was 0.690 g (98.5%). Its semicarbazone melts at 164-165° and fails to be depressed with authentic n-butyl phenyl ketone semicarbazone.

VI. Preparation of the Ethylphenylmethoxybenzoylcarbinol Stereoisomers**

a) Preparation of the α-Isomer. To a solution of phenylmagnesium bromide, prepared from 2 g of magnesium, with cooling was added a solution of 4 g of the methyl ether of the keto alcohol [(II), R=H, R'=C_2H_5]. After heating for 5 hours at ether boil the organomagnesium complex was decomposed with water; the ether was distilled from the ether solution of the reaction product, after which the residue was steam-distilled to remove benzene, excess bromobenzene and diphenyl. The residue was extracted with ether and the ether solution was dried over Na_2SO_4. An oil remained after distilling off the ether, which quickly crystallized. The substance was recrystallized from petroleum ether. M.p. 83°.

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* Work done by S. S. Skorokhodov.

** Work done by A. K. Petryaeva.

Found %: C 79.9, 79.45; H 8.10, 8.07; OCH_3 11.8. $C_{17}H_{20}O_2$. Calculated %: C 79.60, H 7.80; OCH_3 12.1

b) The β-Isomer was prepared in similar manner, starting from 4 g of benzoin methyl ether. From the reaction an oil was isolated, which crystallized only after standing for two weeks. Recrystallized from petroleum ether M.p. 64°.

Found %: C 79.40, 79.56; H 8.30, 8.20; OCH_3 12.0. $C_{17}H_{20}O_2$. Calculated %: C 79.60; H 7.80; OCH_3 12.1.

In conclusion we wish to express our deep gratitude to V. M. Chulanovsky and S N. Andreeva for their advice and assistance in making the infrared spectral studies.

SUMMARY

1. It was shown that the best agent for the isomerization of the methyl lactolides of α-keto alcohols to the methyl ethers of their isomeric α-keto alcohols is zinc chloride. More drastic conditions are required for the isomerization of the methyl lactolides of the tertiary keto alcohols than for the isomerization of the methyl lactolides of the secondary keto alcohols.

2. The methyl lactolides of methylethylbenzoylcarbinol and methyl-n-butylbenzoylcarbinol are new. When these compounds are isomerized with $ZnCl_2$ there occurs shifting (migration) of the hydrocarbon group with the longest hydrocarbon chain; in both cases the methoxy ketones are obtained, containing an acetyl group.

3. The infrared absorption spectra of a number of methyl lactolides of alkylaryl α-keto alcohols were measured, and also of their genetically associated compounds: the ketones, α-keto alcohols, and the isomerization products of the latter – the methyl ethers of the isomeric α-keto alcohols. It was established that a frequency of 917 cm^{-1} is present in the absorption spectra of all of the examined methyl lactolides of alkylaryl keto alcohols, which frequency is characteristic for the α-oxide ring found in the methyl lactolides of the alkylaryl series.

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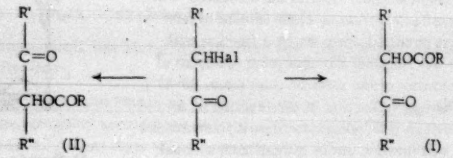
HALOGEN REPLACEMENT REACTIONS IN α-HALOCARBONYL COMPOUNDS

V. THE REACTION OF α-BROMOBENZYL METHYL KETONE WITH THE SALTS OF TRIMETHYLACETIC AND SALICYLIC ACIDS

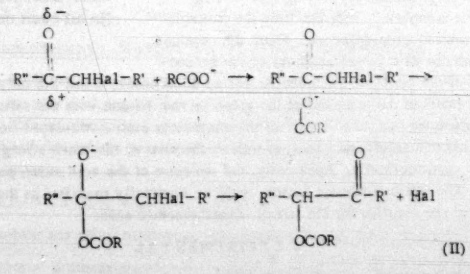
V. I. Veksler

The reaction of α-halo ketones with salts of carboxylic acid is a particular instance of the extremely interesting halogen replacement reactions taking place in α-halocarbonyl compounds and accompanied by molecular rearrangements, which reactions have been studied in detail by A. E. Favorsky and his school [1, 2].

As was shown by T. I. Temnikova [3], in this reaction, together with the ester of the keto alcohol (I), in its structure corresponding to the original halo ketone, there is also formed the anomalous ester (II) – a derivative of the isomeric keto alcohol:



In accordance with the earlier developed representations [4], reaction of the halo ketone with the salt begins with reaction between the anion of the salt and the carbon atom of the carbonyl group; this reaction can lead to the formation of a stable bond between them with subsequent reconstruction of the molecule, as a result of which the ester of structure (II) is formed:

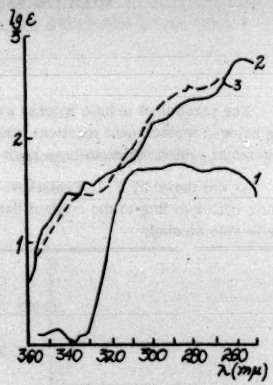


From Temnikova's data it is known [3] that the potassium salt of acetic acid ($K\ 1.82 \cdot 10^{-5}$) with α-bromobenzyl methyl ketone gives mainly the anomalous ester (II), while with the salt of the stronger benzoic acid ($K\ 6.27 \cdot 10^{-5}$) it gives almost entirely the normal ester (I). As a result, it appears that the weaker the corresponding acid, i.e., the more nucleophilic its anion, the greater is the yield of the anomalous reaction product (II). However, the existing data are completely insufficient to make any conclusion as to the exact relationship prevailing between the nucleophilic properties of the anion and the reaction direction.

In the present work we set ourselves the problem of studying the relationship existing between the direction of the indicated reaction and the strength of the acid of the reacting salt; our task was to obtain additional experimental material so that we could judge whether the course of the salt reaction with the given bromo ketone is determined only by the strength of the corresponding acid, or whether other properties of the reactant salt anion also play a part. For this purpose we studied the reaction between α-bromobenzyl methyl ketone, which compound was studied by Temnikova, and the potassium salt of trimethylacetic acid; this acid ($K\ 9.76 \cdot 10^{-6}$) is weaker than acetic

acid and, consequently, if the yield of the anomalous ester is inversely proportional to the strength of the corresponding acid, then here the specific ester (II) should be predominantly obtained. In addition, we also studied the reaction of the same bromo ketone with the sodium salt of the comparatively strong salicylic acid (K $16.5 \cdot 10^{-4}$). In all cases the reaction was run under the previously described conditions [3]: in anhydrous ethyl alcohol solution with heating on the water bath.

The experimental study showed that a crystalline substance with m.p. 74-74.2° is the main reaction product for the salt of trimethylacetic acid. This substance, on the basis of comparing its properties and ultraviolet absorption spectrum with the properties of the authentic isomeric ester (II) – the trimethylacetate of methylbenzoylcarbinol (m.p. 36-37°), should be assigned the structure of the trimethylacetate of phenylacetylcarbinol, i.e., of the normal reaction product (I) [$R' = C_6H_5$, $R'' = CH_3$, $R = C(CH_3)_3$]. The former ester was synthesized from α-bromopropiophenone; its structure is determined by the fact that, as far as is known [3, 4], α-bromopropiophenone with salts of acids forms only the esters that correspond in their structure to the original bromo ketone, i.e., the esters of methylbenzoylcarbinol. Besides the substance with m.p. 74-74.2°, in the studied reaction, a small amount of noncrystallizing product was obtained, from which a fraction with b.p. 160-175° (30 mm) was isolated; the absorption spectrum of the latter is very close to that of the isomeric ester (m.p. 36-37°). Consequently, it must be concluded that in the reaction of α-bromobenzoyl methyl ketone with potassium trimethylacetate the anomalous ester (II) is also formed, but in insignificant amount, in approximately the ratio of 1:10 to the ester of normal structure (I). In the main the reaction proceeds normally.



1) Phenylacetylcarbinol trimethylacetate, m.p. 74-74.2°; 2) methylbenzoylcarbinol trimethylacetate, m.p. 36-37°; 3) noncrystallizing reaction product of α-bromobenzyl methyl ketone with potassium trimethylacetate, b.p. 160-175° (30 mm). (In all cases the solvent was ethyl alcohol).

With sodium salicylate we were able to obtain only one product with m.p. 123.5-124°, which should be considered as being the salicylate of phenylacetylcarbinol (I) ($R' = C_6H_5$, $R'' = CH_3$, $R = o\text{-}OHC_6H_4$), since it is completely different from the isomeric ester synthesized from α-bromopropiophenone. When the obtained results are compared with the data presented above it can be concluded that the strength of the acid (the nucleophilic nature of its anion) is not the only factor determining the formation of anomalous esters in the reactions of the given bromo ketone with the salts of carboxylic acids. If the salt of acetic acid gives not less than 70-80% of the anomalous ester (calculated from Temnikova's data [3]), then the salt of the weaker trimethylacetic acid, as well as the salts of the much stronger benzoic and salicylic acids, for the most part, react normally. Apparently, the structure of the acid anion plays a part here, in particular – steric factors. The steric hindrance factors could be especially manifest in the specific case of their influence on the course of the reaction for the salt of trimethylacetic acid.

EXPERIMENTAL

I. Reaction of α-Bromobenzyl Methyl Ketone with Potassium Trimethylacetate

The salt was prepared according to Butlerov [5]; the bromo ketone was obtained by the bromination of methyl benzyl ketone in glacial acetic acid solution; due to its instability it was not distilled and instead was used freshly prepared, in accordance with the literature indications [3].

Experiment 1. To a warm solution of 21 g of the salt in 80 ml of anhydrous ethyl alcohol was added 25 g of the bromo ketone. Immediately considerable heat was evolved and potassium bromide was precipitated. After heating on the water bath to disappearance of halogen traces the solution was filtered, the alcohol distilled off, water added, and the mixture extracted with ether. After distilling off the ether the reaction product (18.5 g) partially crystallized. The liquid portion was distilled: 1st fraction 90-135° (6 mm), 4.7 g; 2nd fraction 135-180° (6 mm), 4.3 g. When redistilled the 2nd fraction boiled at 124-130° (6 mm), and crystallized. The total yield of crystalline substance was 9.5 g. Recrystallization from petroleum ether gave cohering silky needles, m.p. 74-74.2°. The substance is easily steam-distilled. It fails to be saponified when heated with barium carbonate for 30 hours.

Found %: C 71.32; H 7.55. $C_{14}H_{18}O_3$. Calculated %: C 71.77; H 7.74.

Experiment 2. A mixture of 17 g of the bromo ketone and 15.5 g of the salt in 100 ml of anhydrous alcohol was taken. The heating time was 30 minutes. The potassium bromide was filtered, and the alcohol was vacuum-distilled; the addition of water resulted in immediate crystallization. The crystals were pressed out, washed with water and then with benzene; weight 10.2 g; after recrystallization from light benzene, m.p. 73.5-74°. Fractional crystallization gave only crystals of the same substance with m.p. 72.5° and higher.

After removing the crystals the water layer was extracted with ether; the ether extract was combined with the wash gasoline, dried over sodium sulfate, and the solvent vacuum-distilled. The liquid residue weighed 6 g, which when distilled at 19 mm gave: 1st fraction 65-90°, 1.6 g; 2nd fraction 95-101°, 1.0 g, and residue 3.0 g. The 2nd fraction is mainly original methyl benzyl ketone that had failed to brominate: its semicarbazone, m.p. 183.5-184.5°; the mixed melting point failed to be depressed. The residue (3 g), obtained from the distillation, on standing gave crystals (1.2 g) with m.p. 72.5-73° (from gasoline); fractional crystallization gave the same substance (m.p. 73-74°). The liquid portion of the residue was distilled: from 0.9 g was obtained 0.55 g of the substance with b.p. 160-175° (30 mm), which, on standing gave a minute amount of crystals, melting at 67-69° and, apparently, from the above indicated main crystalline product in impure form.

Judging from its analysis, and absorption spectrum, the fraction with b.p. 160-175° (30 mm) is a heterogeneous substance, apparently being predominantly methylbenzoylcarbinol trimethylacetate.

Found %: C 72.2; H 8.3. $C_{14}H_{18}O_3$. Calculated %: C 71.77; H 7.74.

The total yield of reactionproducts was 11.4 g of crystalline ester and 1.6 g of noncrystalline product, and also 1.6 g of lower boiling fractions.

Preparation of the Isomeric Ester from Potassium Trimethylacetate and α-Bromopropiophenone. A mixture of 9 g of α-bromopropionphenone, obtained according to [6], 9 g of the salt and 50 ml of anhydrous alcohol was taken. After heating and the usual treatment there was obtained on distillation: 1st fraction – to 122° (5 mm), 1.5 g, 2nd fraction 132-142° (5 mm), 2.5 g. After long standing with strong cooling and rubbing with a glass rod both fractions partially crystallized. The total amount of crystalline substance obtained was 1.5 g (of which 1.3 g came from the 2nd fraction). In accordance with the considerations mentioned above the obtained substance is the trimethylacetate of methylbenzoylcarbinol. M.p. 36-37° (from petroleum ether); very readily soluble in all of the common organic solvents.

Found %: C 71.1; H 7.75. $C_{14}H_{18}O_3$. Calculated %: C 71.77; H 7.74.

II. Reaction of α-Bromobenzyl Methyl Ketone with Sodium Salicylate.

A mixture of 25 g of the bromo ketone with 25 g of the salt in 100 ml of anhydrous alcohol was heated for 5 hours. After the usual treatment a dark, crystalline mass was obtained. Despite the use of animal charcoal and various solvents we were able to obtain only sand-colored crystals. M.p. 123.5-124° (from alcohol); the substance is difficultly soluble in the cold in petroleum ether, ether and ethyl alcohol, and easily soluble in chloroform, acetone and benzene.

Found %: C 71.8, 71.9; H 5.1, 4.9. $C_{16}H_{14}O_4$. Calculated %: C 71.10; H 5.22

We were unable to isolate any other substances from the reaction products by fractional crystallization.

The Isomeric Ester from α-Bromopropiophenone was obtained by heating 3.5 g of the salt and 2.5 g of the bromoketone in anhydrous alcohol solution for 10 hours. A while, crystalline substance with m.p. 77-78° (from alcohol) was obtained.

I consider it my pleasant duty to express deep gratitude to T. I. Temnikova for her valuable advice in performing the present work.

SUMMARY

The reaction of α-bromobenzyl methyl ketone with potassium trimethylacetate gave mainly the normal reaction products – the ester of phenylacetylcarbinol, and in insignificant amount the isomeric ester, corresponding to methylbenzoylcarbinol. We were unable to show the presence of the isomeric ester of methylbenzoylcarbinol in the reaction with sodium salicylcate.

In this way it was established that the direction of the reactions between bromo ketones and salts of carboxylic acids is not determined by the strength of the corresponding acids, but instead depends on their structure.

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HYDROLYSIS OF ALGINIC ACID AND DERIVATIVES OF D-MANNURONIC ACID

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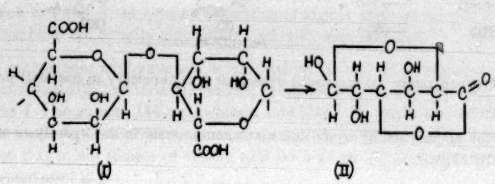
The polyuronide—alginic acid, found [1] in the laminarian and fucaceous types of brown marine algae (White Sea, Pacific Ocean coast, etc.), can serve as the starting material for the synthesis of various substances, especially as the result of its hydrolysis. On the basis of studying this and other polyuronides (pectic substances) it was shown [2], including the x-ray study method [3], that the alginic acid molecule is built of anhydromannuronic acid (pyranose) units, linked by γ-glucosidic 1,4-bonds, and having the general formula: $H(C_6H_8O_6)_nOH$ or $H[C_5H_5O_2(OH)_2\text{-}COOH]_nOH$.

From the literature [4] the molecular weight of alginic acid is above 100,000, $n > 500$.

When we hydrolyzed alginic acid (I) by various techniques we obtained [5] in satisfactory yields the already known γ-mannuronolactone $C_6H_8O_6$ (II) and some previously unknown derivatives of D-mannuronic acid.



(I) (II)

The hydrolysis of alginic acid proceeds slowly, possibly due to the stability of the pyranosido-β-uronido bond, the influence of the carboxyl group, the structure of the material, and also because the hydrolysis is complicated by the fact that it is impossible to appreciably raise either the concentration or temperature of the hydrolytic agent for fear of cleaving carbonic acid [6] at the expense of the carboxyl groups and the reversion reaction.

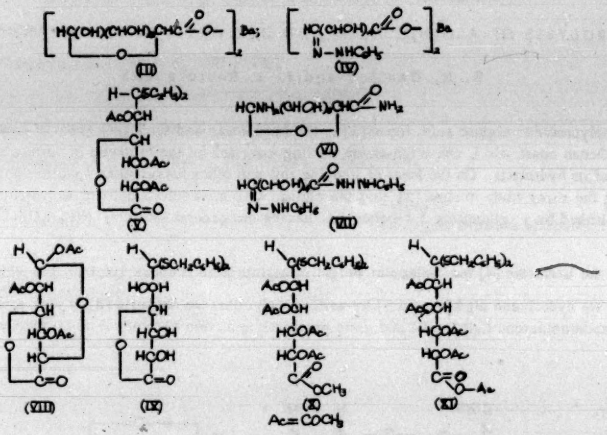
Under mild conditions the hydrolysis fails to go to completion, in which connection low-molecular polysaccharides remain in the hydrolysis products. The tendency shown by alginic acid for incomplete hydrolysis is explained by some authors as being due to the existance [6] of two forms of polymannuronic acids (high resistance and low resistance to hydrolysis), which existance has not been proved.

Recently, the kinetics for the hydrolsys of alginic acid with mineral and organic acids was studied [7]. Some authors ran the hydrolysis of the alginic acid in aqueous medium with dilute mineral acids [6] but failed [1] to obtain sufficiently good yields of mannuronic acid or its lactone. The hydrolysis products were isolated [6] as the cinchoninic or barium salts or even as the crystalline acid and its lactone (V. V. Ronzhina and N. A. Pribytkova in A. I. Vedrinsky's book [1]). The hydrolysis was worked successfully if the alginic acid was subsequently treated with sulfuric acid, with concentrated acid under cooling, or with highly dilute acid under heating [8]

In our experiments on the hydrolysis of alginic acid we used mineral acids in alcohol medium as the hydrolytic agent, by analogy with the hydrolysis of polygalacturonide [9]. The alcoholysis products in the presence of hydrochloric acid were isolated by us either as the barium salt or as the diethylthio derivative.

Methanolysis in the presence of sulfuric acid failed to give successful results, since the separation of the barium salts of mannuronic acid from the barium salts of methylthiotartaric acid was difficult.

Considerable success in the preparation of mannuronolactone was achieved in our experiments if the hydrolysis of the alginic acid with formic acid was run in several stages, in contrast to the literature indications in Spoer [10], who proposes a one-step technique for the hydrolysis with formic acid.



As was shown in our experiments, for successful hydrolysis it is necessary to use well pulverized alginic acid (Samples 2 and 3, Table 1).

Below we describe the preparation of crystalline mannuronolactone in the hydrolysis of alginic acid and also of some mannuronic acid derivatives.

EXPERIMENTAL

1. Preparation of the Samples

Sodium alginate, the starting substance for our experiments, was obtained from the Archangel Agar-Agar Plant (1951). A 1% sodium hydroxide solution or a 2% soda solution was used to extract the product from the marine algae (seaweed). In drying the sodium alginate it was observed that the somewhat over-dried samples had the appearance of thin (0.1-0.3 mm in thickness) dark-brown sheets with a white deposit of salts. The product was analyzed for the amount of mineral residue, which, for example, was 12.11% when analyzed for sodium, while the theoretical amount should have been 11.60% Na. In addition to sodium, the mineral portion contained compounds of silicon, calcium, manganese and iron. The sodium alginate samples showed a reducing action when treated with Fehling solution.

Mineral acids are usually used to isolate alginic acid from sodium alginate, since of the organic acids only the stronger ones combine with the sodium of sodium alginate (for example, formic and oxalic acids, but not acetic acid).

The alginic acid obtained in this manner is contaminated with ash, dye pigments, etc. Various methods have been described for the isolation and purification of alginic acid [2, 4]; after purification such preparations contain 0.2-0.5% ash and are destroyed to greater or lesser degree.

Our experiments on the isolation of alginic acid from the sodium salt, using 20% hydrochloric acid with a 2-fold precipitation and subsequent washing, failed to give favorable results, since we obtained a highly hydrated gel (74% water) that could be dehydrated only with difficulty (even with 99% methyl alcohol); when dried a dense solid mass was formed that was difficult to pulverize and showed low reactivity.

Better results were obtained when the dry sodium alginate, ground in a ball mill and sifted to a fine powder, was treated with an alcohol solution of hydrochloric acid. The samples were first dried in the air and then in vacuo (5 mm) at 50-60° over dehydrating agents.

The obtained alginic acid samples were analyzed for their ash content, neutralization equivalent, amount of anhydromannuronic acid, and reducing properties.

The alginic acid samples are characterized in Table 1. For determining the neutralization equivalent of alginic acid the theory required for the titration of 1 g of pure alginic acid is 55.8 ml of 0.1 N sodium hydroxide solution, which corresponds to a neutralization equivalent of 179, but most authors find these determinations to be quite variable.

TABLE 1

Analyses (average) of Alginic Acid from the White Sea Laminaria Kelps (Seaweed)

Sample Nos.	Conditions of Alginic Acid Treatment	Amount (in %)		Neutralization Equiv.	Am't of mannuronic units (in %)	$[\alpha]_D^{20}$
		Ash	Iron in Ash			
1	Without additional purification	1.95	–	236	74.6	–
2	Allowed to stand with 0.5% hydrochloric acid for 48 hours, extracted with methyl alcohol	0.38	0.23	234	74.5	−138.7
3.	Allowed to stand with 0.5% hydrochloric acid for 72 hours and extracted with methyl alcohol	0.25	0.16	233	75.6	−136.3

In our data, given in Table 1, an aqueous suspension of alginic acid was titrated in the presence of phenolphthalein, in which connection abnormally high values (233-237) were obtained.

The amount of mannuronic acid units was determined on the basis of their cleavage with the separation of carbon dioxide [determined with baryta water (barium hydroxide solution)] and furfurol (furfural) under the conditions of heating for 4-5 hours with 18% hydrochloric acid [11]. The amount of uronic acids was as high as 75%, which corresponds to the found neutralization equivalent (236) and yield of alginic acid (71%) from sodium alginate. It can be seen that in our sample of alginic acid the acid groups were partially decarboxylated and the molecules were depolymerized [12].

For the samples, purified by steeping with 0.5% hydrochloric acid and removing the pigments by extraction with methyl alcohol (pale yellow powder with an ash content of 0.4%), the neutralization equivalents and other characteristics differed but slightly when compared with the same properties for less purified samples. The rotation of the plane of polarization of our samples of alginic acid corresponded to that given in the literature [6]. The optical rotation changes as a function of the temperature and time of drying the alginic acid. The rotation for the sample of alginic acid was determined after its exact neutralization with dilute sodium hydroxide solution, i.e. it was determined in the form of sodium alginate.

2. Methanolysis of Alginic Acid with Hydrogen Chloride

The experiments on the methanolysis of alginic acid were run in the presence of 3 and 5% hydrogen chloride in alcohol solutions (for 90 hours), where simultaneous hydrolysis and esterification of the alginic acid proceeded with the formation of the methyl ester of methyl-γ-mannuroside, remaining in solution. The incompletely hydrolyzed polyuronide was separated as a gelatinous mass. In the methanolysis with a 3% hydrogen chloride solution about 50% of the taken alginic acid went into solution, and about 60% in the presence of a 5% hydrogen chloride solution.

Experiment 1. The postulated methyl ester of methyl-γ-mannuroside was obtained as a sirup. For each experiment there was taken 100 g of alginic acid (ash content 0.27%) and 1 kg of dry methyl alcohol, which had been previously saturated with hydrogen chloride to a 3% content (by weight). The solution was heated at the boil with constant stirring on the water bath for 9 days of 10 hours each. The mixture was vacuum-filtered through a cloth filter; after long drying the slimy precipitate weighed 50.3 g. The solution was decolorized with activated carbon. To remove hydrogen chloride and alcohol the solution was concentrated in vacuo (at 200 mm) at a bath temperature of 35° with alternate addition of methyl alcohol and its distillation in admixture with hydrogen chloride until a sirup completely devoid of hydrogen chloride was obtained, which sirup failed to crystallize even after standing in a refrigerator for 6 days.

The sirup was hydrolyzed by heating for 8 hours in a 4% aqueous hydrochloric acid solution until a constant angle of rotation had been established, in which connection a very small amount of light brown precipitate was obtaine . The hydrochloric acid was removed with silver carbonate, while the silver salt of mannuronic acid was decomposed with hydrogen sulfide.

Barium Salt $(C_6H_9O_7)_2Ba$ (III). The mannuronic acid was isolated as the barium salt by treatment with barium carbonate, the solution of the barium salt being decolorized by treatment with activated carbon (Norit). Most of the water was removed in vacuo, the temperature of the solution being kept around 30-35° to avoid decomposition of the barium salt. To the lemon-yellow solution after cooling (4°) was added 95% methyl alcohol (10-15 ml per 100 ml of solution) to precipitate the unhydrolyzed polyuronides, which operation was repeated several times to achieve more complete fractional precipitation. The residual solution was poured into 5 volumes of cold 95% methyl alcohol with stirring, where the barium salt of mannuronic acid separated, which after standing for 3 hours at −5° was filtered and washed with anhydrous methyl alcohol. The salt briquette was suspended in dry ether. The drying of the barium salt was completed in a vacuum-desiccator over calcium chloride. The yield of salt was 60.5 g, which corresponds to 90% of the alginic acid that had gone into solution. The salt decomposes around 180°.

For analysis a weighed sample of barium mannuronate $(C_6H_9O_7)_2Ba$ was dried in a vacuum tube over phosphorus pentoxide at 50-60° and 5 mm.

Analysis (average of three determinations) gave in %: Ba 26.30. $(C_6H_9O_7)_2Ba$. Calculated %: Ba 26.26.

Rotation of the plane of polarization (0.4274 g of barium mannuronate in 25 ml of water) $[\alpha]_D^{20}$ 3.51°. Literature [13]: $[\alpha]_D^{25}$ 4.0−4.5°.

Phenylhydrazone of the Salt (IV). Barium D-mannuronate when reacted with phenylhydrazine in a medium of aqueous acetic acid and barium acetate under the usual conditions (0.6 g of freshly distilled phenylhydrazine, 12 ml of water, 3.5 ml of 50% acetic acid, 1.45 g of the mannuronate and 6.0 g of barium acetate) forms the phenylhydrazone of the barium salt, which, after mixing the reactants, settles within 3-4 minutes as a heavy, granular, pale-yellow precipitate. The precipitate failed to change when 30 ml of 95% ethyl alcohol was added. After standing for 12 hours at −4° the solution was filtered. The precipitate was washed with water, then with 95% ethyl alcohol for complete removal of the phenylhydrazine, and then dried by washing with anhydrous alcohol and dry ether (44% of the theoretical yield was obtained).

The phenylhydrazone of barium mannuronate as a yellow powder is insoluble in water, alcohol and ether, and when heated it fails to melt, but decomposes above 200° with gas evolution.

When analyzed, the vacuum-dried substance gave in % (average of two determinations): Ba 19.46; N 7.80; C 40.83; H 4.32. $C_{24}H_{30}O_{12}N_4Ba$. Calculated %: Ba 19.53; N 7.96; C 40.94; H 4.23.

Experiment 2. The alcoholysis was run for 90 hours in anhydrous methyl alcohol with 5% dry hydrogen chloride. The treatment of the solution was the same as in Experiment 1. The sirup of the postulated methyl ester of the methylglucoside failed to crystallize after standing for 7 days at −4°.

Acetylation of the sirup (postulated methyl ester of methylmannuronide) with acetic anhydride in the presence of zinc chloride with short heating at 60-70° failed to give a crystalline acetate. The sirupy acetate is insoluble in water. After filtering from the hydrolysis products, the slimy precipitates, being the methyl ester of the methylglucoside of polymannuronic acid, were dried and analyzed, where it was found in %: ash 0.28; OCH_3, 16.37.

With water the substance gave viscous solutions, which confirmed its high molecular weight.

Mercaptalation of the Sirup. Since the sirup failed to crystallize, a part of it (22 g) was dissolved at 2° in 30 ml of concentrated hydrochloric acid (d 1.18), which should have caused the hydrolysis of the methyl mannuronate methylglucoside; to the solution was added 20 ml of ethyl mercaptan. The mixture was shaken in a flask for 5 hours at room temperature and each hour it was cooled for 15 minutes with an ice-salt mixture. The reaction mixture was poured into 200 ml of ice water, the oily layer was separated, and the aqueous layer extracted with ether. After removal of the ether the resulting thick sirup (11 g) was kept in a crystallizer (in a desiccator over sodium hydroxide) cooled to −50°, but the substance failed to crystallize.

An attempt was made to obtain the methyl mannuronate mercaptal from the postulated mannuronolactone mercaptal. For this the sirupy mercaptal was dissolved in 5 parts of anhydrous methyl alcohol, in which dry hydrogen chloride had been dissolved (roughly a 1 N solution); the solution was heated at the boil for 30 minutes, which caused it to darken, and then the hydrogen chloride and alcohol were removed in vacuo. The substance remained sirupy.

Acetate of the Mercaptal (V). The noncrystalline ethyl mercaptal (presumably of mannuronolactone, due to the hydrolysis of the methyl ester of the methylglucoside in the mercaptalation carried out in the presence of aqueous hydrochloric acid) was acetylated with acetic anhydride in pyridine solution at room temperature. After 18 hours the mixture was poured into water, the separated sirupy substance was extracted with chloroform, then freed of chloroform

and decolorized in alcohol solution with activated carbon at room temperature. Evaporation of the solution gave crystals in a yield of 7% on the weight of sirup (2.7 g from 11.5 of sirupy mercaptal), while the remainder failed to crystallize, since, as can be seen, the acetylation was insufficiently complete. After recrystallization from anhydrous methyl alcohol the crystals were obtained as colorless prisms with a length of about 15 mm; m.p. 103-104°, which remained constant after a second recrystallization.

The substance is readily soluble in alcohol, ether and chloroform, but is insoluble in water.

Analysis of the carefully dried substance revealed it to be the triacetate of mannuronolactone ethyl mercaptal (V).

Rotation of the plane of polarization: $[\alpha]_D^{17.5}$ +36.20° (in chloroform, c 1.9428).

The substance analyzed (average of two determinations) in %: C 46.68; H 5.76; S 15.55. $C_{18}H_{24}O_9S_2$. Calculated %: C 47.06; H 5.88; S 15.68.

As a result, the fact that barium mannuronate and its phenylhydrazone were obtained, and also the triacetate of mannuronolactone ethyl mercaptal, serves as evidence that in the methanolysis the reaction went to the final hydrolysis product.

3. Hydrolysis with Formic Acid

The use of formic acid for hydrolyzing alginic acid is to be preferred over the use of mineral acids for the reason that the decarboxylation and reversion reactions are diminished). In addition, the removal of the mineral acid from the reaction mixture is a troublesome operation. Hydrolysis with formic acid makes it possible to immediately obtain the crystalline mannuronolactone from the hydrolysis products. We introduced certain improvements in running the hydrolysis with formic acid (according to Spoer), which permitted us to raise the yield of pure crystalline lactone: 1) the use of well-purified (freed of ash and coloring substances) and pulverized alginic acid; 2) running the hydrolysis in several steps, taking into consideration the fact that in the hydrolysis of polysaccharides the usual sequence is formation of the monose and then its decomposition, and also that the uronic acids are even less stable than the monosaccharides; 3) to avoid the precipitation of incompletely hydrolyzed polymannuronic acids on the mannuronolactone crystals it is advisable not to wash the crushed (triturated) mannuronolactone crystals with an alcohol-acetone mixture. As was shown in our experiments, an alcohol-acetone mixture precipitates flocculent yellow precipitates of polymannuronic acids from the hydrolysis solutions. Stepwise hydrolysis reduces the degree of hydrolyzate darkening when formic acid is used, which darkening is observed even in a carbon dioxide atmosphere, and also lessens the accumulation of mannuronic acid reversion products and alginic acid decarboxylation products. The product from each hydrolysis step was isolated separately.

Using an ash-containing (2%) alginic acid and the Spoer method, we were unable to obtain a pure mannuronolactone; the isolated product (in 40% yield on the amount of uronic acids) had a wide melting range (m.p. 126-139°); the unhydrolyzed residue exceeded 44%.

Well crystallized, pure mannuronolactone is obtained in satisfactory yields if the stepwise hydrolysis method is used, which procedure is favorable for retarding the decomposition of the formed lactone under the conditions of heating with formic acid (90%). Alginic acid (with an ash content of 0.2-0.3%) was hydrolyzed with 90% formic acid in 4-6 steps, in which connection each hydrolysis step was run under analogous conditions, but for different periods of time, and where after each step the crystalline lactone was separated from the reaction mixture.

For the first hydrolysis step it is expedient to heat for 6 and not more than 8 hours, under which conditions the most complete cleavage of the polyuronide is achieved. With a longer heating period for the first step a large amount of residue is formed as the result of reversion and decarboxylation, which residue fails to give the lactone later.

The subsequent hydrolysis steps are run by heating the sirup, obtained after removal of the lactone crystals and evaporation of the filtrate in vacuo, with a 15-fold amount of formic acid for various periods of time (most frequently from 1.5 to 2.5 hours). The hydrolyzate was usually colored a brown, dark-brown and even black color, especially in the last hydrolysis stages. A shorter heating period facilitates obtaining a less colored hydrolyzate. To decolorize the hydrolyzate it is necessary to use activated carbon that had been steam treated (Norit). After removal of the formic acid by distillation the hydrolyzate was decolorized by dissolving the obtained sirup in methyl alcohol and shaking (with Norit) at room temperature. At times, due to decomposition of the product, a light, brown flocculent precipitate was noticed in the alcohol solution, which further failed to hydrolyze, especially on prolonged heating.

The formic acid and alcohol were vacuum-distilled at a bath temperature of 40-50°. The residue after the removal of formic acid was treated twice with methyl alcohol, which also was removed by distillation under reduced pressure. Following the completion of these steps, The sirup was dissolved in methyl alcohol and, as already indicated, the solution was decolorized with carbon. In isolating the lactone from the sirup it is advisable to replace the methyl alcohol by ethyl alcohol, since the γ-mannuronolactone is more difficultly soluble in the latter.

The sirup crystallized either spontaneously or by rubbing the sides of the beaker with a glass rod. For crystal growth the product was kept in a refrigerator at −5°.

A large number of experiments on the multiple-step hydrolysis was run under various conditions. The yields of crystalline lactone were as high as 50-70% of the total amount of uronic acids present in the alginic acid. A glycerine bath served as the heat source in our experiments, where the temperature was raised to the constant boiling of 90% aqueous formic acid, which, however, appears to be too drastic, judging from a certain accumulation of brown precipitates, which proved to be both insoluble and incapable of hydrolysis. To keep the precipitate from hitting the bottom of the flask it is advisable to put some beads in the vessel.

The reaction course was controlled by analyzing the precipitates for the amount of uronic acids (from the amount of carbonic acid) and by determining the neutralization equivalent.

For the sake of illustration in Table 2 are given the results of a 6-step hydrolysis of alginic acid (50 g), where in all cases a crystalline lactone with m.p. 139-140-141° was isolated.

TABLE 2

Step	Experimental Conditions		Unhydrolyzed Residue (in g)	Weight of Sirup (in g)	Yield of Lactone (in g)
	90% Formic Acid (in ml)	Duration of Hydrolysis (in Hours)			
1	800	6	3.30	–	10.4
2	435	1.5	–	34.8	4.2
3	350	1.5	–	27.7	3.3
4	270	1.5	–	21.3	1.9
5	225	1.5	–	18.4	1.4
6	180	1.5	–	15.0	1.1
Final products	–	–	–	11.80	22.3

The formic acid needed for the experiments was obtained from the technical grade (85%) by the method of drying it with boric anhydride (from boric acid in an electric furnace), distillation (b.p. 101°, d^{20} 1.22), and dilution with water to 90% (d 1.045).

The material that was subjected to formic acid hydrolysis was the sirupy alcoholysis product (in methyl alcohol in the presence of 3-5% hydrogen chloride), which hypothetically was the methylglucoside of methyl D-mannuronate. It can be assumed that when this product is heated with dilute formic acid the methylglucoside group is hydrolyzed and the ester group is decomposed [17]. 83% Aqueous formic acid was used and the experiment was run in 4 steps. The yield of isolated mannuronolactone (m.p. 141°) was 53% of the amount of uronic acids present in the alginic acid. These experiments of the hydrolysis of the methylglucoside of methyl mannuronate with formic acid in essence failed to differ from those on the direct hydrolysis of alginic acid with formic acid.

D-Mannuronolactone (II). It was recommended earlier [6, 13] to recrystallize the lactone from hot acetic acid. In our experiments the lactone was recrystallized from hot water; here the hydrolysis of any esters of formic acid, that might be present in the lactone in minute amounts, should have been effected. After one recrystallization the lactone (colorless prisms) was obtained with m.p 143-144°, which remained the same after a second recrystallization, and with $[\alpha]_D^{20}$ 92.84° (after 30 minutes, in water), which is close to the literature data [6]. The formula is supported by the analytical data. The lactone is readily soluble in water, soluble with considerably more difficulty in methyl and ethyl alcohols, and insoluble in cold alcohol, acetone and ether.

4. Derivative of D-Mannuronic Acid

All of the derivatives of mannuronic acid, which, due to their crystallinity, can serve for characterizing the

hydrolysis products of alginic acid and for characterizing synthetic mannuronic acid [14], have still not been sufficiently studied.

1-Aminomannuronamide (VI). We obtained this compound by treating D-mannuronolactone with a methyl alcohol solution of ammonia. This substance crystallizes as snow-white prismatic crystals, but fails to have a sharp melting point, decomposing around 145° with the evolution of gaseous products. An aqueous solution (mutarotatory) after 10 minutes had $[\alpha]_D^{18.5}$ −49.86°, while in the literature [8] a value of $[\alpha]_D^{20}$ −50.85° is indicated. For the barium salt of mannuronic acid the preparation of the aminoglucoside proceeds with extremely great difficulty, both in liquid and in aqueous ammonia, due to the insolubility of the salt in both media.

Phenylhydrazide of D-Mannuronic Acid Phenylhydrazone (VII). γ-Mannuronelactone (m.p. 143°) was dissolved in the minimum amount of hot water, ethyl alcohol was added, and this solution was mixed with 4 weight parts of freshly distilled phenylhydrazine (b.p. 120° at 12 mm) in alcohol solution. The mixture was heated for 10 minutes on the steam bath. The solution on cooling began to deposit white scale crystals. The filtered crystals were washed with anhydrous ethyl alcohol and then with ether. The yield was 80% of the theoretical. The snow-white crystals had m.p. 164°, and after 2 recrystallization from 80% ethyl alcohol had m.p. 166° (with some decomposition).

The substance had: $[\alpha]_D^{18}$ +14.68° (in pyridine).

Analysis (average of three determination) gave in %: C 57.81; H 6.15; N 15.12. $C_{18}H_{22}O_5N_4$. Calculated %: C 57.75; H 5.88; N 14.97.

The substance must be regarded as being the phenylhydrazide of D-mannuronic acid phenylhydrazone.

Triacetyl-D-mannuronolactone (VIII) was synthesized from 3 g of the lactone, which was added with stirring to 15 ml of acetic anhydride in the presence of a small lump of fused zinc chloride. The lactone slowly dissolved and the mixture was heated for 20 minutes on the water bath at 60-70°. After standing for 12 hours the mixture was poured into ice water and the sirupy substance extracted with chloroform, the removal of which in vacuo gave as residue an amber yellow sirup (5.8 g), which gradually crystallized when rubbed with a glass rod. The yield of crystalline substance with m.p. 119° was 2.2 g (42%). After recrystallization from hot 99% ethyl alcohol the substance had m. p. 119-120° (without decomposition), $[\alpha]_D^{20}$ +139.84° (in dry chloroform).

Analysis (average of two determinations) gave in %: C 47.40; H 4.82. $C_{12}H_{14}O_9$. Calculated %: C 47.69; H 4.67.

Mannuronolactone Diethylmercaptal and its Triacetate (V). These compounds, as already indicated, obtained from the alcoholysis products, can also by synthesized from the pure D-mannurono-γ-lactone, which fact confirms the formation of mannuronic acid and its lactone during alcoholysis. The ethyl mercaptan was synthesized in known manner [15] from thiourea; the isolation of the product was modified in this respect: the ethyl mercaptan was immediately distilled through a long Vigreaux column into a receiver, cooled with an ice-water mixture, in a stream of carbon dioxide. The ethyl mercaptan had b.p. 37°.

To a solution of 2 g of the lactone (m.p. 143-144°) in 12 ml of approximately 1 N hydrogen chloride in alcohol solution was added 2.0 ml of ethyl mercaptan. The mixture was let stand at room temperature for 1.5 hours, and then it was heated for 30 minutes under reflux at a slight boil. The hydrogen chloride was removed by vacuum distillation with alcohol (alcohol was added twice). The yield of sirup was 3 g, which failed to crystallize at −4°, the same as for the alcoholysis products.

To obtain the crystalline acetate the sirup was treated with acetic anhydride in pyridine, as has already been described above. The yield of crystalline mannuronolactone ethyl mercaptal triacetate was 2.5 g (54%). After recrystallization from hot anhydrous alcohol the substance (as long rod-like colorless crystals) had m.p. 103-104° (without decomposition), as was already indicated. $[\alpha]_D^{25}$ 36.72° (in anhydrous methyl alcohol), which is close to the value for the sample obtained in the alcoholysis.

Found %: C 47.17; H 6.10; S 15.79. $C_{16}H_{24}O_8S_2$. Calculated %: C 47.06; H 5.88; S 15.68.

D-Mannuronolactone Dibenzyl Mercaptal (IX). Benzyl mercaptan was prepared from benzyl chloride and thiosulfate [16]. By using more concentrated sulfuric acid (60%) we were able to obtain (in a stream of carbon dioxide) yields in excess of 80%. B.p. 78° (5 mm), n_D^{18} 1.5768.

To prepare the benzyl mercaptal 5 g of D-mannuronolactone was dissolved in 7.5 ml of concentrated hydrochloric acid with shaking in a flask, 7.5 ml of benzyl mercaptan was added, and the mixture was shaken for 5 minutes at room temperature. The reaction mixture was poured into ice water, the mercaptal was filtered through a

glass filter, and then it was again introduced into water to which benzene had been added. The treatment was repeated twice. The product was again filtered and then dried in a desiccator over potassium hydroxide and paraffin. The yield was 10 g (80%). M.p. 42-43°. For purification the product was dissolved in anhydrous ethyl alcohol, the solution filtered, and the alcohol vacuum-distilled. The light yellow sirup failed to crystallize in the desiccator over calcium chloride and paraffin; it immediately solidified when water was added. The filtered and dried colorless powder had m.p. 44-45° (without decomposition). The substance is soluble in anhydrous methyl and ethyl alcohols, chloroform, acetone, pyridine, ether and carbon tetrachloride.

$[\alpha]_D^{17.5}$ +125.0° (in methanol), $[\alpha]_D^{19.5}$ +124.87° (in methanol).

Found %: C 58.97; H 5.63; S 15.40. $C_{20}H_{22}O_8S_2$. Calculated %: C 59.11; H 5.41; S 15.75.

Methyl 2,3,4,5-Tetraacetyl-D-mannuronate Dibenzyl Mercaptal (X). If a solution of 2 g of the lactone in 12 ml of 1 N hydrogen chloride solution in anhydrous methyl alcohol is treated with 2.8 g of benzyl mercaptan, then, after letting the solution stand for 1.5 hours at room temperature and heating for 30 minutes in a flask under reflux, apparently the benzyl mercaptal of methyl mannuronate is formed. Removal of the alcohol and hydrogen chloride in vacuo gave 5 g of sirup as residue. To obtain a crystalline product the sirup was acetylated in anhydrous pyridine with acetic anhydride, the latter being added in small amounts and with cooling of the mixture. The reaction and isolation conditions were the same as for the acetylation of the mannuronolactone ethyl mercaptal. After pouring into water the mixture was extracted with chloroform, which was then vacuum-distilled, but crystallization failed to ensue.

The sirupy product was dissolved in anhydrous methyl alcohol, the solution decolorized with activated carbon (Norit) at room temperature, and the alcohol removed by evaporation in vacuo. The obtained sirup was again dissolved with heating in a small amount of anhydrous methyl alcohol. Crystallization began when the solution was cooled. The yield of substance was 2.4 g (35%), m.p. 95-96° (without decomposition); after recrystallization from anhydrous methyl alcohol and cooling, the substance immediately crystallized as colorless rods with m.p. 96-97°. The substance is readily soluble in methyl alcohol and acetone, more difficulty in benzene, and insoluble in water; $[\alpha]_D^{21}$ + 164.94° (in chloroform).

Found %: C 57.08; H 5.51; S 10.90 (average of three analyses) $C_{29}H_{34}O_{10}S_2$. Calculated %: C 57.42; H 5.61; S 10.56.

Acetylation of Mannuronolactone Dibenzyl Mercaptal (XI). By analogy with the synthesis of triacetylmannuronolactone diethyl mercaptal (V), it was postulated to obtain the triacetylmannuronolactone benzyl mercaptal by acetylation. However, it was revealed that the acetylation failed to stop at the benzyl mercaptal triacetate stage. It can be seen that further there was cleavage of the lactone ring with the addition of acetic anhydride to the lactone ring, since the mixed anhydride of tetraacetylmannuronic acid benzyl mercaptal (X) was formed. It can be assumed that the presence of benzyl groups in the mercaptan radicals facilitated the weakening of the lactone ring.

The reaction was run in the following manner: 10 g of D-mannuronolactone dibenzyl mercaptal (m.p. 44-45°) was dissolved in 35 ml of anhydrous pyridine and to the solution was added with stirring and cooling 45 ml of freshly distilled acetic anhydride. The reaction mixture was kept for about 1 hour at 0°, and then for 18 hours at room temperature (where the solution became somewhat yellow), after which it was poured into ice water and extracted after some time with chloroform, which was then vacuum-distilled at 25-30°. For its complete decolorization the obtained sirup in methyl alcohol solution was well shaken with activated carbon (Norit) at room temperature; the methyl alcohol was removed in vacuo, leaving a sirup, which only partially crystallized on long standing; consequently, the sirup (14.8 g) was acetylated a second time under the above described conditions and isolated as in the previous experiment. After removal of the chloroform the sirup began to crystallize; the addition of anhydrous methyl alcohol facilitated more complete crystallization. After two recrystallizations of the crude (m.p. 144-145°) from boiling anhydrous methyl alcohol there was observed on cooling a copious separation of crystals as fine white needles, the melting point of which had risen to 147-149°. The yield of substance was 8.8 g (57%). The product is readily soluble in acetone, chloroform and ether, and more difficultly soluble in hot ethyl and methyl alcohols; $[\alpha]_D^{21.5}$ +99.93°.

Found %: C 56.85; H 5.16; S 10.17 (average of three determinations). $C_{30}H_{34}O_{11}S_2$. Calculated %: C 56.78; H 5.36; S 10.00.

From this product we were unable to obtain, first, the phenylhydrazide of the acid when treated with phenylhydrazine in alcohol medium, and, second, the esters of the acid when heated with anhydrous methyl alcohol or with the same alcohol in the presence of small amounts of pyridine. The absence of reactivity can be explained by the stability and low solubility of this complex acid anhydride.

SUMMARY

1. For the preparation of alginic acid it is advisable to treat the previously pulverized sodium alginate with an aqueous hydrochloric acid solution. For liberation from ash and pigments the product as a friable powder is steeped with 0.5% hydrochloric acid solution, followed by extraction with methyl alcohol.

2. The best results for the hydrolysis of alginic acid were obtained under the conditions of heating at the boil in 90% aqueous formic acid in several steps, in which connection the pure D-mannurono-γ-lactone is isolated. This method is the surest of all for obtaining the pure mannuronolactone. The isolation of the mannuronolactone is made much more difficult under the conditions of alcoholysis in the presence of hydrogen chloride. The products were characterized as the barium salt, the phenylhydrazone of this salt, and the triacetate of the diethyl mercaptal.

3. A number of crystalline derivatives of D-mannuronic acid and of its lactone were obtained, which derivatives are convenient for both identification and isolation purposes.

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CYCLOHEXANE COMPOUNDS OF MONOSES

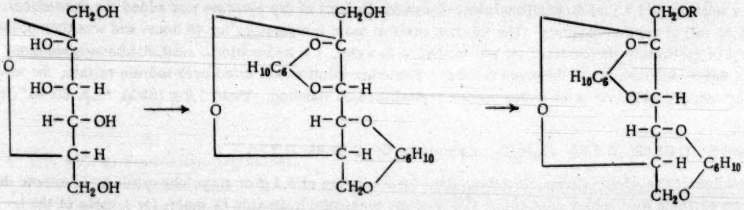
II. DICYCLOHEXYLIDENE-L-SORBOSE

V. F. Kazimirova

Earlier [1] well crystallized compounds of xylose, arabinose and sorbose with cyclohexanone were described, but their structures were not proved. Dicyclohexylideneglucose, synthesized by Hochett and coworkers [2], has a structure similar to that of diacetoneglucose. It can also be assumed that dicyclohexylidene-L-sorbose and diacetone-L-sorbose are identical in structure.

Diacetone-L-sorbose, and also its oxidation product, diacetone-2-keto-L-gulonic acid, were described by Reichstein and Grüssner [3]. The transformation of diacetone-2-keto-L-gulonic acid into L-ascorbic acid has been described in detail in the literature and has been effected by different investigators under various conditions – in aqueous medium and in solutions of inert organic solvents [4]. V. M. Berezovsky and L. I. Strelchunas [5] studied the transformation of diacetone-2-keto-L-gulonic acid into L-ascorbic acid under the influence of mineral acids in the presence of chloroform of dichloroethane and established the transformation mechanism. V. I. Veksler and G. E. Shaltyko [6] studied the transformation rate of diacetone-2-keto-L-gulonic acid into ascorbic acid in aqueous medium and determined the rate constants for the formation and decomposition of L-ascorbic acid.

Our present investigation problem was to study the structure of dicyclohexylidene-L-sorbose and to synthesize its derivatives. In the previous investigation it was shown that L-sorbose (I) condenses with two molecules of cyclohexanone, after which it contains only one free alcohol (hydroxyl) group. In the present study we describe the synthesis of monobenzoyldicyclohexylidene-L-sorbose (III) and acetyldicyclohexylidene-L-sorbose (IV):

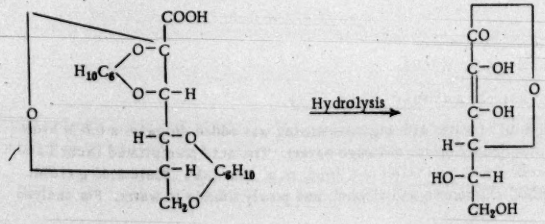


(I) (II)

(III) R=COC_6H_5, (IV) R=$COCH_3$, (V) R=$C(C_6H_5)_3$.

(III, IV, V)

It can be concluded that it is the primary alcohol group that remains free, since only primary alcohols enter into reaction with triphenylchloromethane. Dicyclohexylidene-L-sorbose was oxidized with potassium permanganate in pyridine solution, where the potassium salt of dicyclohexylidene-2-keto-L-gulonic acid (VI) was isolated, the aqueous solution of which with dilute hydrochloric acid gave crystalline dicyclohexylidene-2-keto-L-gulonic acid (VI).



(VI) (VII)

The hydrolysis of dicyclohexylidene-2-keto-L-gulonic acid with hydrogen chloride in the presence of chloroform and 95% ethyl alcohol gave ascorbic acid (VII).

EXPERIMENTAL

1-Benzoyl-2,3:4,6-dicyclohexylidene-L-sorbose (III)

To a solution of 1.4 g of dicyclohexylidene-L-sorbose (II) in 10 ml of dry pyridine with cooling was added 0.7 g of benzoyl chloride. The mixture was shaken for a short time and let stand for a day at room temperature. Then ice water was added; an oil was obtained that solidified on cooling. The substance was dissolved in 20 ml of chloroform, the chloroform solution thoroughly washed with ice water, then with cooled 1 N hydrochloric acid, 5% soda solution, water, and dried over anhydrous sodium sulfate. The chloroform was removed under reduced pressure; the solid residue of 1.4 g (77.7%) was recrystallized from alcohol.

M.p. 101–102°, $[\alpha]_D^{23}$ −19.5° (in benzene, c 2.69)
Found %: C 67.30, 67.21; H 7.20, 7.24. M 431. $C_{25}H_{32}O_7$. Calculated %: C 67.56; H 7.20. M 444.

1-Trityl-2,3:4,6-dicyclohexylidene-L-sorbose (V)

To a solution of 1.7 g of dicyclohexylidene-L-sorbose in 15 ml of dry pyridine was added 1.4 g of triphenylchloromethane. The mixture stood for 48 hours at 37°, after which 100 ml of ice water was added; here an oil was obtained that solidified on cooling. The amorphous mass was thoroughly washed with ice water and dissolved in 30 ml of ether. The ether solution was dired over anhydrous sodium sulfate and the ether evaporated at room temperature. The residue as a viscous mass was treated twice with ether, washed with methyl alcohol, and dried Yield 1 g (30.3%), m.p. 122-123°.

$[\alpha]_D^{22}$ −29.0° (in benzene, c 1.45)
Found %: C 76.43, 76.39; H 7.11, 7.25. $C_{37}H_{42}O_6$. Calculated %: C 76.29; H 7.22.

1-Acetyl-2,3:4,6-dicyclohexylidene-L-sorbose (IV)

To a solution of 1.7 g of dicyclohexylidene-L-sorbose in 5 ml of dry pyridine was added the theoretical amount (0.55 ml) of acetic anhydride. The mixture stood at room temperature for 48 hours and was then poured into 100 ml of ice water; the obtained oil was washed with water, 1 N hydrochloric acid, dilute soda solution, again with water, and then it was dissolved in ether. The ether solution was dried over sodium sulfate, the solvent removed by suction, while the thick sirupy residue crystallized on standing. Yield 1.2 g (63%), m.p. 63-65° (from alcohol).

Found %: C 63.06; H 7.90. $C_{20}H_{30}O_7$. Calculated %: C 62.82; H 7.85.

Oxidation of Dicyclohexylidene-L-sorbose (II). To a solution of 5.1 g of dicyclohexylidene-L-sorbose in 25 ml of dry pyridine were added solutions of 1.58 g of dry potassium hydroxide (2 moles for 1 mole of the L-sorbose) in 7.5 ml of water and 4.75 g of potassium permanganate (2 moles for 1 mole of the L-sorbose) in 100 ml of water. The mixture was stirred for 12 hours and then was heated on the water bath for 30 minutes. After cooling the manganese dioxide precipitate was filtered and washed with water, which was then added to the solution. The solution was saturated with carbon dioxide gas and then shaken twice with ether (to remove the original compound), after which the water was removed under reduced pressure at 50°. To the dry residue was added 65 ml of anhydrous alcohol, the solution was filtered, and the solvent was removed by suction. After recrystallization from alcohol the potassium salt of dicyclohexylidene-2-keto-L-gulonic acid was obtained as tiny colorless needles; the salt was washed with absolute ether and dried in a vacuum-desiccator. Yield 5.02 g (85%). The salt is extremely hygroscopic.

$[\alpha]_D^{22}$ −15.9° (in water, c 1.14).
Found %: K 9.65. $C_{18}H_{25}O_7K$. Calculated %: K 9.94.

2,3:4,6-Dicyclohexylidene-2-keto-L-gulonic Acid (VI)

To a solution of 3.5 g of the salt in 8 ml of water with vigorous stirring was added dropwise a 0.5 N hydrochloric acid solution (the reaction was controlled by means of Congo paper). The acid precipitated immediately; the crystalline precipitate was filtered, washed with cold water and dried, m.p. 129-131°. Yield 2.45 g (75%). The acid is readily soluble in benzene, ether, chloroform and alcohol, and poorly soluble in water. For analysis the acid was well dried in vacuo [7].

$[\alpha]_D^{22}$ −28.3° (in methanol, c 1.12).

Found %: C 60.67, 60.87; H 7.63, 7.41. $C_{18}H_{27}O_7$. Calculated %: C 61.01;

The Hydrolysis of Acid (VI) was run in anhydrous medium. A solution of 1 g of the acid in 2.5 ml of chloroform and 0.5 ml of 94% ethyl alcohol was saturated with hydrogen chloride and then heated at 60° for 5 hours. The precipitate was washed with chloroform and a mixture of chloroform with alcohol. The ascorbic acid (VII) was determined by titration with iodine. Yield 32%.

SUMMARY

1. The previously unknown crystalline compounds were synthesized: 1-benzoyl-2,3:4,6-dicyclohexylidene-L-sorbose, 1-acetyl-2,3:4,6-dicyclohexylidene-L-sorbose, and 1-trityl-2,3:4,6-dicyclohexylidene-L-sorbose.

2. The oxidation of 2,3:4,6-dicyclohexylidene-L-sorbose gave 2,3:4,6-dicyclohexylidene-2-keto-L-gulonic acid, the hydrolysis of which gave ascorbic acid.

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* T.p. = C. B. Translation pagination.

TAUTOMERIC COMPOUNDS

XIX. THE TAUTOMERISM OF DIPYRAZOLONYL-m-NITROPHENYLMETHANE

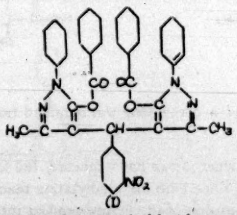
A. E. Porai-Koshits,* B. A. Porai-Koshits and N. G. Lipina

In previous communications [1-3] some conclusions were made on the structure and transformations of the condensation products of 1-phenyl-3-methyl-5-pyrazolone with aromatic aldehydes. Studied in greatest detail were the condensation products of 1-phenyl-3-methyl-5-pyrazolone with m- and p-nitrobenzaldehydes.

It was established that the reaction of 2 moles of the pyrazolone with 1 mole of aldehyde results in the formation of two products – a white and a yellow, identical in composition, but differing in their properties and melting points. The mutual transitions of the white and yellow products in solutions and under temperature variations, in combination with the identity of the elementary compositions and equality of the molecular weights of the white and yellow substances, and also the bromine titration results for these two products, gave basis to assume that these two substances are tautomeric. The white substances are tautomeric. The white substances, in accord with their properties, were characterized as being the enolic, while the yellow substances were postulated as being the ketonic tautomers.

Continuing our work in the indicated direction, we obtained on the example of studying the compound dipyrazolonyl(m-nitro-phenyl)methane some new evidence of the validity of the above expressed postulation that the structure of the white product corresponds to the enol form, and established that the structure of the yellow product corresponds to the keto form, in this way confirming the keto-enol tautomerism of the dipyrazolonyl(m-nitrophenyl)methane.

Thus, when the white product was reacted with benzoyl chloride we obtained the dibenzoyl derivative of the white product: bis[1-phenyl-3-methyl-5(benzoyloxy)-4-pyrazolyl](3-nitrophenyl)methane (I):



(I)

When the yellow product was reacted with benzoyl chloride we obtained the same compound (I) as in the case of the white product, since here the reaction proceeded under conditions that were favorable for the tautomeric transition of the yellow product into the white.

A study of the infrared absorption spectra of the white product (as a powder) revealed that its absorption spectrum contains bands with a frequency corresponding to that of enol groups.

Consequently, both the benzoylation results and the spectroscopic study results support an enolic structure for the white product.

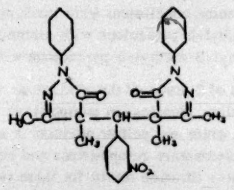
As regards the yellow product, we were unable to confirm its ketonic structure by the method of preparing derivatives in which the reactivity of the carbonyl group is involved, in all probability for the reason that the carbonyl group present in this compound lies closer in its character to the co-group of acyl radical than it does to a keto group, and acyl derivatives, as is known, fail to show reactions that are characteristic for the carbonyl

* Deceased.

group. However, when the yellow product as a powder was studied in the infrared region it was found that its absorption spectrum contains bands with a frequency corresponding to that of carbonyl groups.

Of interest for demonstrating the presence of tautomerism for the white and yellow products was the result of their methylation, which also served at the same time as proof of the ketonic structure of the yellow product.

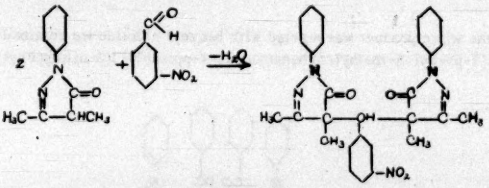
It is known that the methylation of sodioenol derivatives of the type of sodioacetoacetic ester leads, as a rule, apparently, on the principle of reaction center transfer [4], to the formation of C-methyl derivatives. Proceeding from this, it could be expected that in the reaction of methyl iodide with the sodio derivative of the white product we would obtain the dimethyl derivative of the latter, namely, bis(1-phenyl-3,4-dimethyl-4-pyrazolonyl)(3-nitrophenyl)methane (II):



(II)

The experimental data justified our expectations: the methylation of the white product gave the methylation product of the yellow substance, insoluble in alkalis.

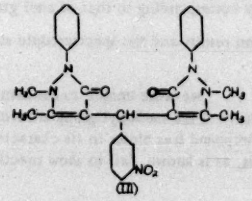
The structure of the methylation product, besides the analyses, was confirmed by its synthesis from 3,4-dimethyl-1-phenyl-5-pyrazolone and m-nitrobenzaldehyde by the scheme:



In turn, the 3,4-dimethyl-1-phenyl-5-pyrazolone was obtained from the C-methylacetoacetic ester and phenylhydrazine.

The methylation of the yellow product, as we had expected, led to the same compound (II) as was obtained in the methylation of the white product, since here the methylation reaction was run under the same conditions as are used for realizing the tautomeric transition of the yellow product into the white.

If the yellow product existed in the imino form, then as the result of methylation we should have isolated the compound 4,bis(1-phenyl-2,3-dimethyl-4-pyrazolinyl)(3-nitrophenyl)methane (III):



(III)

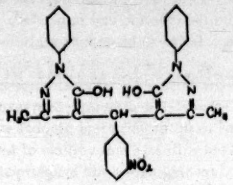
The fact that the same product is obtained in the methylation of the yellow substance as is obtained for the while product serves as indirect evidence that the yellow product is not the imino form, and consequently, it is the keto form of the dipyrazolonyl compound.

Since the tautomerism in the case of the dipyrazolonyl(m-nitrophenyl) methane is associated with hydrogen transition, then, naturally, the presence of two substances should not be observed in the compounds where this hydrogen atom is substituted in any way.

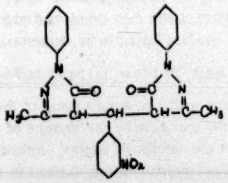
Actually, as was experimentally shown, for both the above described compound (II) and its specially synthesized and in detail studied isomer (III) it was established that each of them exists only in one form. The same was also true for the case of attempting to isolate more than one form of bis(1-phenyl-3-methyl-4-bromo-4-pyrazolonyl) (3-nitrophenyl)methane [3].

As a result, the above presented data support the validity of the earlier made conclusions on the presence of keto-enol tautomerism for the dipyrazolonyl(m-nitrophenyl)methane. This is also supported by the spectroscopic study data obtained for solutions of the white and yellow products. Made in different solvents, the latter study revealed that in solvents we are not dealing with solutions of individual substances, but instead with equilibrium mixtures of both substances, where the character of the solvent influences the shift in the direction of either predominantly the white or the corresponding yellow form. Thus, the absorption spectra of the white and yellow products in alcohol solution, the same as for the white and yellow products in acetic acid, have correspondingly similar characteristics (see EXPERIMENTAL).

From all of the above it follows that the white product represents the enolic tautomer, bis(1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl)(3-nitrophenyl)methane.



The yellow product represents the ketonic tautomer, bis(1-phenyl-3-methyl-4-pyrazolonyl)(3-nitrophenyl)-methane.



EXPERIMENTAL

I. Benzoylation of the White and Yellow Dipyrazolonyl-(m-nitrophenyl)methanes*

To a slightly heated suspension of 3 g of the white product (m.p. 150°) in 30 ml of 96% ethyl alcohol was added 2 ml of concentrated sodium hydroxide solution. After cooling 1.5 ml of benzoyl chloride was added to the mixture. After some time a copious precipitate of crystalline sodium chloride was obtained, which was immediately filtered. From the filtrate, with slight water dilution, a white, finely crystalline product with m.p. 165° was isolated. Yield 3.6 g. After 3 recrystallizations from 96% alcohol, m.p. 171°.

* The preparation of the white and yellow dipyrazolonyl-(m-nitrophenyl)methanes was described in detail earlier [3].

Found %: C 71.31; H 4.62; N 10.18, 10.30. $C_{41}H_{31}O_4N_5$. Calculated %: C 71.50; H 4.50; N 10.16.

The product is insoluble in alkalis and soluble in most organic solvents, including ethyl and methyl alcohols, acetone, acetic acid, etc.

One gram of the yellow product (m.p. 227°) was benzoylated as described above for the benzoylation of the white product. From the reaction a product with m.p. 171° was isolated. The mixed melting point with the benzoyl derivative of the white product failed to be depressed.

Methylation of the White and Yellow Dipyrazolonyl-(m-nitrophenyl)methanes

To a suspension of 2.5 g of the white product (m.p. 150°) in 25 ml of anhydrous methyl alcohol was added in drops a solution of 1.5 g of metallic sodium in 5-10 ml of anhydrous methyl alcohol, after which 6 ml of methyl iodide was gradually introduced. The resulting mixture was heated on the water bath in a small flask under reflux until the reaction showed neutral to phenolphthalein paper. Then the sodium iodide was filtered, and the excess methyl iodide and two-thirds of the alcohol removed by distillation. The residue on cooling deposited a yellow product. M.p. 177°. Yield 1 g. After recrystallization from a small volume of methyl alcohol, m.p. 178°.

Found %: C 68.5, 68.0; H 5.2, 5.6; N 13.89. $C_{29}H_{27}O_4N_5$. Calculated %: C 68.40; H 5.3; N 13.79.

Acidification of the filtrate gave another 1.1 g of product as the hydrochloride. M.p. 140°.

The methylation product (m.p. 178°) is readily soluble in alcohol and acetic acid, and insoluble in alkalis, benzene, toluene and water. When recrystallized from acetone it crystallizes with one mole of acetone. When the product with one mole of acetone is boiled with water the acetone of crystallization is lost.

One gram of the yellow product (m.p. 227°) was methylated under the same conditions as for the methylation of the white product. The product isolated from the reaction had m.p. 178°. Its mixed melting point with the product from the methylation of the white substance failed to be depressed.

Condensation of 1-Phenyl-3,4-dimethyl-5-pyrazolone with m-Nitrobenzaldehyde

To a solution of 1.88 g (0.01 mole) of 1-phenyl-3,4-dimethyl-5-pyrazolone (m.p. 119-120°) and 0.75 g (0.005 mole) of m-nitrobenzaldehyde (m.p. 57-58°) in 15 ml of 96% ethyl alcohol was added 8 ml of concentrated hydrochloric acid and the resulting solution was diluted with an equal volume of hot water. The mixture was boiled in an open beaker for 20 minutes. On cooling and rubbing with a rod a light-yellow product separated, melting at 140°, which product is the hydrochloride of the dimethyl derivative of the white product. Yield 65%. The obtained product was placed in a beaker, treated with an aqueous solution of calcined soda, and it aqueous suspension boiled for 10-15 minutes. The product turned yellow during the boiling process. After separation from the filtrate, the product, thoroughly washed with water and with alcohol and then dried, had m.p. 178°. The mixed melting of this product with the dimethyl derivative of the white product failed to be depressed.

Spectroscopic Study of the White and Yellow Dipyrazolonyl-(m-nitrophenyl)methanes

A quartz spectograph of medium dispersion with a hydrogen lamp of the Popov system was used to measure the absorption spectra in the ultraviolet region of the spectrum by the method of variable thickness layers. The method of "threshold blackening" was used to construct the absorption curves. Anhydrous ethyl alcohol and glacial acetic acid were used as the solvents. The measurement results are summarized in the curves given below in Fig. 1.

An infrared spectrometer of the "Hilger" firm was used for the measurements in the infrared portion of the spectrum. The light source was an incandenscent nichrome filament. The absorption spectra of suspensions of the powdered product in paraffin oil were measured.

From an examination of the curves shown in Fig. 2 it follows that the white product (I) has an absorption band with a frequency of 3550 cm^{-1}, which is characteristic for the enol group, while for the yellow product such an absorption band is absent. On the other hand, the yellow product (II) has an absorption band with a frequency of 1720 cm^{-1}, which is characteristic for the carbonyl group, and which is absent in the white product.

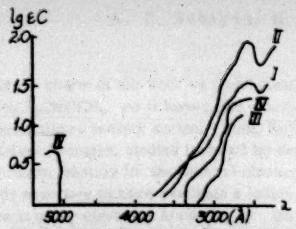


Fig. 1. Absorption Spectra in the Ultraviolet Region. I) white product in alcohol, II) yellow product in alcohol, III) white product in acetic acid, IV) yellow product in acetic acid.

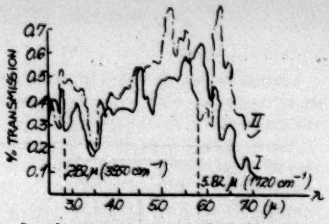


Fig. 2. Absorption Spectra in the Infrared Region. I) white product, II) yellow product.

SUMMARY

The spectroscopic studies of solutions of the white and yellow dipyrazolonyl(m-nitrophenyl)methanes, combined with the data of their benzoylation and methylation, demonstrate the presence of keto-enol equilibrium between these two forms. The white product is the enol form, while the yellow product is the keto form of dipyrazolonyl(m-nitrophenyl)methane.

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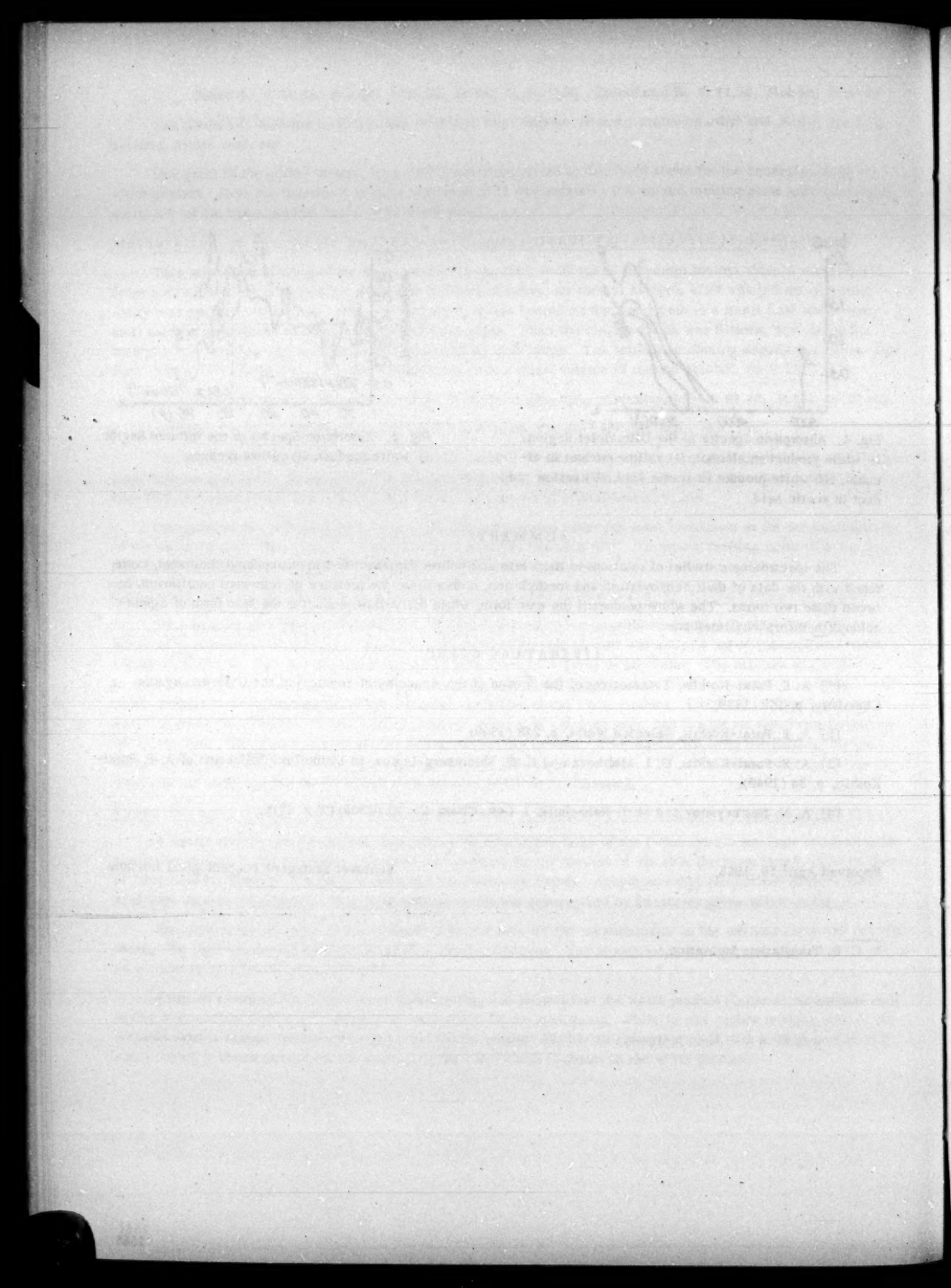
* C. B. Translation pagination.



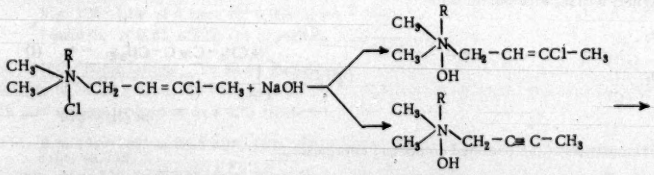
THE CLEAVAGE OF QUATERNARY AMMONIUM BASES

I. SYNTHESIS OF MIXED TERTIARY AMINES

A. T. Babayan, N. G. Vartanyan and I. Ya. Zurabov

In the course of our work we found ourselves in need of some mixed tertiary amines of the general formula $R'(R'')NCH_2C{\equiv}CCH_3$. As is known, the reaction for the cleavage of quaternary ammonium bases can be used for the synthesis of mixed tertiary amines. Thus, for example, the reaction for the cleavage of quaternary ammonium salts with nascent hydrogen, studied in detail by Emde [1], was used by him for the synthesis of mixed tertiary amines. The Hofmann reaction for the thermal cleavage of quaternary ammonium bases can also be used in similar manner. It is only necessary to have available a halide derivative of such an alkyl, the bond of which with the ammonium nitrogen is easily cleaved. According to the studies of Braun [2], in quaternary ammonium bases the benzyl and allyl radicals are cleaved with especial ease.

Working with amines and quaternary ammonium bases containing the 3-chlorobutenyl radical, we determined the bond stability of this radical with the ammonium nitrogen. By analogy with the allyl and benzyl radicals it could be expected that it would be easily cleaved. To elucidate this problem we heated both dimethylallyl(3-chlorobutenyl) ammonium bromide and dimethylbenzyl(3-chlorobutenyl) ammonium chloride with aqueous alkali. Vigorous gas formation resulted when the reaction mixture was heated to 80-90°; in both cases the tertiary amine was obtained, minus the 3-chlorobutenyl radical, and respectively, dimethylallylamine and dimethylbenzylamine. The nitrogen-free portion of the cleavage product in both cases proved to be a mixture of chloroprene and monovinylacetylene. The presence of monovinylacetylene in the reaction products indicates that there is also partial dehydrochlorination of the 3-chlorobutenyl radical, preceding cleavage. Apparently, the reaction proceeds in accord with the following scheme:



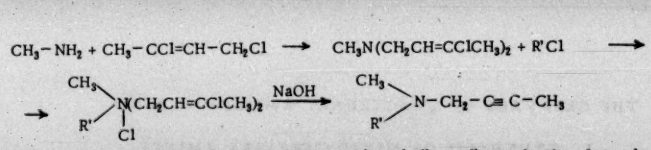
$$\longrightarrow \quad \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!N-R + CH_2=CH-C{\equiv}CH + CH_2=CCl-CH=CH_2 + H_2O$$

$$R = -CH_2-CH=CH_2,\ -CH_2-C_6H_5.$$

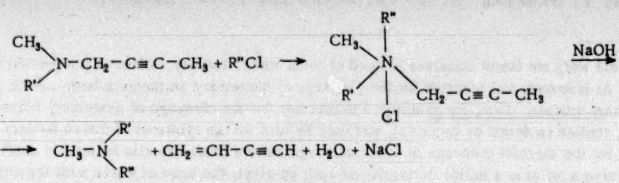
The formation of monovinylacetylene as the result of the cleavage of the butynyl radical was also observed by G. M. Mkryan [3] in the heating of ethers of 2-butyn-1-ol with alkalis. The absence in the reaction products of tertiary amines, containing either the 3-chlorobutenyl or butynyl radical, speaks of the exclusive ease with which these radicals cleave at the 1,4-position to yield systems with conjugated multiple bonds.

We used this property of the indicated radicals to realize the synthesis of the mixed tertiary amines in which we were interested. For this purpose the reaction of methylamine with 1,3-dichloro-2-butene gave us the starting methyldi(3-chlorobutenyl)amine [4]. Then, by reaction with the desired alkyl halide we obtained the corresponding quaternary salt. The heating of this salt with an aqueous alkali solution resulted in the removal of only one of the 3-chlorobutenyl radicals. Here the second 3-chlorobutenyl radical in alkaline medium suffered dehydrochlorination. As a result the β-dialkylaminobutyne was obtained.

The reaction proceeds in accord with the following scheme:

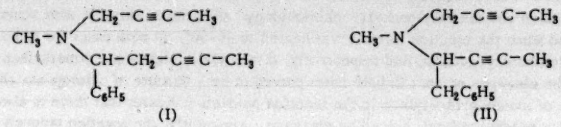


In this way we obtained methylethylbutynylamine and methylbenzylbutynylamine. Later, by adding a second halide derivative and heating the resulting quaternary ammonium salt with aqueous alkali, it is possible to replace the butynyl radical by a different radical:

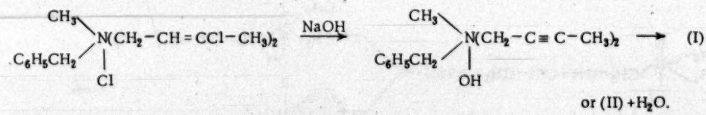


Thus, for example, we obtained methylethylbenzylamine in this manner.

When methylbenzyldi(3-chlorobutenyl)ammonium chloride is heated in aqueous alkali medium, together with methylbenzylbutynylamine, there is also formed a higher boiling substance, which, judging from preliminary data, is a tertiary amine with the structure of either (I) or (II):



These compounds could have been formed as the result of dehydrochlorination and intramolecular carbon-alkylation of the original tertiary ammonium salt:



The structure elucidation of the obtained compound continues.

EXPERIMENTAL

Cleavage of Dimethylallyl(3-chlorobutenyl)ammonium Bromide. To 25 g of dimethylallyl(3-chlorobutenyl)-ammonium bromide with heating on the boiling water bath was added a solution of 14 g of sodium hydroxide in 30 ml of water. The temperature of the reaction mixture was 86-87°. The temperature of the escaping vapors failed to exceed 40-45°. In the receiver 7.8 g of substance was collected, in the gasometer 1.5 liters of gas (680 mm, 17°); the latter with ammoniacal silver oxide solution gave a white precipitate of explosive character, and with Ilosvaya's solution it gave a yellow precipitate. The liquid, collected in the receiver, was treated with hydrochloric acid. The insoluble portion was separated and dried. The yield of chloroprene was 1.6 g, b. p. 56–58° at 680 mm, d_4^{20} 0.9492, Cl 40.02%; on standing in a sealed ampule it polymerized.

Treatment of the hydrochloric acid solution with alkali gave the free dimethylallylamine with b.p. 58–60° at 680 mm; picrate m.p. 112°. From the literature [5] picrate m.p. 100°.

Found %: C 42.19; H 4.65. $C_{11}H_{14}O_7N_4$. Calculated %: C 42.35; H 4.45.

Cleavage of Dimethylbenzyl(3-chlorobutenyl)ammonium Chloride. To 78 g of dimethylbenzyl(3-chlorobutenyl)ammonium chloride with heating on the boiling water bath was added a solution of 36 g of sodium hydroxide in 100 ml of water. The mixture was stirred occasionally. The heating was continued until the low boiling substances ceased to distil. In the receiver, cooled with an ice-salt mixture, was collected 10.5 g of liquid, consisting

of monovinylacetylene and chloroprene. From the reaction mixture was obtained 32 g of amine, b.p. 170-172° at 680 mm, picrate m.p. 94.5-95°; the mixed melting point of the picrate with the picrate of dimethylbenzylamine failed to be depressed.

Methylethylbutynylamine. To 213.8 g of methylethyldi(3-chlorobutenyl)ammonium bromide [obtained by heating a mixture of methyldi(3-chlorobutenyl)amine with ethyl bromide on the water bath] was gradually added 96 g of sodium hydroxide as a 40% aqueous solution. An oil bath was used for the heating. The temperature of the reaction mixture varied from 116 to 122°. Simultaneously with cleavage there occurred distillation of the reaction products with a small amount of water. The top layer of the distilled liquid, together with the ether extract of the bottom layer, was dried and distilled. The yield of methylethylbutynylamine was 57.6 g (77.4%).

B.p. 133–135° at 680 mm, d_4^{20} 0.8165, n_D^{20} 1.4397, MR_D 35.8; calc. 36.46.
Found %: N 12.9. $C_7H_{13}N$. Calculated %: N 12.61.

There was also obtained 5.8 g of methylethyl(3-chlorobutenyl)amine.

B.p. 152–155° at 680 mm, d_4^{20} 0.9316, n_D^{20} 1.4529, MR_D 42.78; calc. 42.86.
Found %: N 9.51. $C_7H_{14}NCl$. Calculated %: N 9.49.

Methylbenzylbutynylamine. To 167.25 g of methylbenzyldi(3-chlorobutenyl)ammonium chloride [obtained by heating 104 g of methyldi(3-chlorobutenyl)amine with 63.25 g of benzyl chloride on the water bath] was gradually added 72 g of sodium hydroxide as a 40% aqueous solution.

An oil bath was used for the heating. The temperature of the reaction mixture remained below 102°. Two layers were formed. The heating was terminated when gas evolution ceased. The upper layer of the reaction mixture and the ether extract of the lower layer were dried, and after distilling off the ether, were distilled. The yield of methylbenzylbutynylamine was 52.7 g (61%).

B.p. 115–116° at 7.5 mm, d_4^{20} 0.951, n_D^{20} 1.521, MR_D 55.393; calc. 55.953.
Found %: N 8.29. $C_{12}H_{15}N$. Calculated %: N 8.09.

There was also obtained 14.5 g of substance, boiling at 138–160° at 3 mm. A second distillation gave 9.56 g of substance.

B.p. 138–140° at 3 mm, d_4^{20} 0.99074, n_D^{20} 1.5553.
Found %: N 6.61. M222 (by titration). $C_{16}H_{19}N$. Calculated %: N 6.22. M225.

Methylethylbenzylamine. To 42.84 g of methylethylbenzylbutynylammonium bromide (obtained by heating a mixture of 26.27 g of methylbenzylbutynylamine and 25 g of ethyl bromide on the water bath) was gradually added 16 g of sodium hydroxide as a 40% aqueous solution. The yield of substance from the reaction was 13.2 g.

B.p. 100–105° at 25.5 mm, 187–190° at 680 mm, d_4^{20} 0.9215, n_D^{20} 0.9215, n_D^{20} 1.5068, MR_D 48.10; calc. 48.719.

Picrate m.p. 113.5–114.5° (from alcohol). The literature gives for methylethylbenzylamine the following data: b.p. [6] 194–196°, 85–87° at 10 mm; picrate m.p. 113° [7].

SUMMARY

1. It was established that quaternary ammonium salts containing either the 3-chlorobutenyl or butynyl radical are easily cleaved when heated with aqueous alkali.

2. It was shown that the ease of cleavage of the 3-chlorobutenyl and butynyl radicals can be successfully used for the synthesis of mixed tertiary amines.

3. The new methylethylbutynylamine, methylethyl(chlorobutenyl)amine and methylbenzylbutynylamine were synthesized.

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SYNTHESES WITH ACRYLONITRILE

XXII. NEW METHOD FOR THE SYNTHESIS OF PYRROLINES

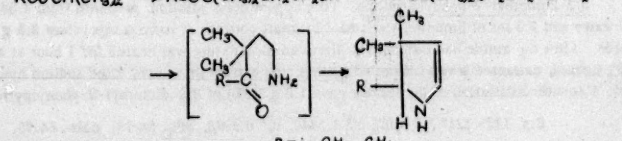
A. P. Terentyev, A. N. Kost, and A. M. Berlin

A. P. Terentyev and M. A. Volodina [1] described the preparation of some pyrrolines and pyrrolidines by the reaction of the δ-oxo alcohols with ammonia or formamide. Pyrrolines can also be easily obtained by the cyclization of γ-amino ketones [2], but the amino ketones themselves are comparatively difficult to obtain.

We used δ-oxo nitriles, which are easily obtained by the reaction of ketones with acrylonitrile, for the synthesis of δ-oxo amides. The latter immediately gave pyrrolines by the Hofmann rearrangement. This method for the synthesis of pyrrolines is not described in the literature (apparently, for the reason that earlier the δ-oxo amides were difficultly available). In only the two studies of Rinkes [3] was the formation of the pyrrole ring under Hofmann rearrangement observed; however, the starting substance used by Rinkes was not the oxo amide, but instead the diamide of polyamide of β-methylmuconic acid. The method proposed by us permits the synthesis of very difficultly available pyrrolines, including the gem-substituted derivatives.

As starting substances we took diisopropyl ketone and isobutyrophenone, from which the corresponding oxo nitriles were obtained. The Radzishevsky method [4] was used to saponify the nitriles to the amides, i.e. by the action of a 3% hydrogen peroxide solution in alkaline medium. The γ-methyl-γ-isobutyrylvaleramide and γ-methyl-γ-benzoylvaleramide obtained in this manner (in nearly quantitative yields), when reacted with sodium hypobromite in aqueous medium, were respectively converted to 3,3-dimethyl-2-propyl-(2)-pyrroline (70% yield) and 3,3-dimethyl-2-phenylpyrroline (58% yield). In both cases the picrates obtained from the ether extracts immediately after running the reaction and the picrates obtained from the already isolated pyrrolines proved to be identical, i.e. cyclization of the γ-amino ketones proceeds readily even during their formation.

Pyrrolines with a C=N double bond have not been described in the literature; always the presence of the C=C double bond was established due to the extreme ease of isomerization. In our case the molecular refraction data and the formation of N-phenylureido derivatives (under the influence of phenyl isocyanate) also speak in favor of finding the double bond between the carbon atoms. As a result, the given method leads, apparently, to the formation of 2,3,3-trisubstituted pyrrolines with the double bond in position 4 (since due to the presence of gem-substitution it is impossible to have the double bond in position 2). In the case of 3,3-dimethyl-3-propyl-(2)-pyrroline it can also be assumed that a semicyclic double bond is present; this assumption, however, is not valid for the case of 3,3-dimethyl-2-phenylpyrroline.



EXPERIMENTAL

γ-Methyl-γ-isobutyrylvaleramide. Sodium ethylate (0.6 g of sodium in 10 ml of anhydrous alcohol) solution was added to 91.2 g of diisopropyl ketone (b.p. 123-124° at 747 mm), after which with constant stirring and heating on the water bath was added in drops 21.2 g of acrylonitrile in 1.5 hours. The mixture acquired a yellow color and a small amount of precipitate was formed. With maintenance of stirring the mixture was heated on the water bath for another 3 hours, then cooled, neutralized with 2 N sulfuric acid (here the precipitate dissolved), and dried over calcined sodium sulfate. After removal of unreacted material by distillation the residue was vacuum-distilled. The yield of γ-methyl-γ-isobutyrylvaleronitrile was 31.5 g (46%).*

* Under the earlier described [4, 5] conditions (equimolar amounts of acrylonitrile and ketone with alcoholic caustic as the catalyst) the yield failed to exceed 28%. If to 0.28 mole of diisopropyl ketone and 2 ml of 40% aqueous sodium hydroxide solution there is added 0.38 mole of acrylonitrile at room temperature (1 hour), and then the mixture heated with stirring on the water bath (80°) for 3 hours, the yield is 20-22%.

B.p. 106–108° at 4 mm, 116–118° at 7 mm, n_D^{20} 1.4432, d_4^{20} 0.9222, MR 48.10; calc. 48.21
Lit.: 125.5–126° at 10 mm[5], 128–129° at 10 mm [6], n_D^{20} 1.4435 [6], n_D^{25} 1.4428 [7], d_4^{20} 0.9226 [6].

In a three-necked flask, fitted with stirrer, reflux condenser and thermometer, was placed 300 ml of 3% hydrogen peroxide solution, 15 g of γ-methyl-γ-isobutyrylvaleronitrile, 3 ml of 6 N sodium hydroxide solution, and sufficient ethyl alcohol to form a homogeneous solution (about 50 ml). Then with stirring the mixture was heated for 6 hours at 50-60°, cooled, neutralized (to litmus) with 2 N sulfuric acid, and evaporated in a dish on the water bath. The semiliquid mass crystallized when cooled. After removing the small amount of mother liquor, washing the precipitate with ice water, and drying in a vacuum-desiccator there was obtained 14.6 g (89%) of γ-methyl-γ-isobutyrylvaleramide, m.p. 82-83°. Recrystallization from anhydrous benzene gave tetrahedral prisms with m.p. 90°.

Found %: C 64.44, 65.08, H 10.28, 10.58. $C_{10}H_{19}O_2N$. Calculated %: C 64.28;

γ-Methyl-γ-benzoylvaleramide. To 7.0 g of γ-methyl-γ-benzoylvaleronitrile (B.p. 159–161° at 4.5 mm, n_D^{20} 1.5200, d_4^{20} 1.0469, MR_D 58.44; calc. 58.46), obtained by the cyanoethylation of isobutyrophenone [6], was added 175 ml of 3% hydrogen peroxide solution, sufficient ethyl alcohol for complete homogeneity of the mixture, and 1.75 ml of 6 N aqueous sodium hydroxide solution. The obtained solution was heated with vigorous stirring on the water bath for 4 hours at 50-60°. After cooling the mixture was neutralized with 2 N sulfuric acid and then evaporated on the water bath in vacuo. The bulky white precipitate obtained on cooling was separated and dried in a vacuum-desiccator. The yield of γ-methyl-γ-benzoylvaleramide was 7.1 g (93.5%). After recrystallization from water, m.p. 145°. Poorly soluble in cold water and soluble in benzene.

Found %: N 6.21, 6.32, 6.45. $C_{14}H_{17}O_2N$. Calculated %: N 6.39.

3,3-Dimethyl-2-propyl-(2)-pyrroline. To a solution of 23 g of sodium hydroxide in 300 ml of water, cooled to −3°, was added 5.5 ml of bromine. Then with stirring 14.2 g of γ-methyl-γ-isobutyrylvaleramide was introduced and the mixture heated under reflux with stirring for 2 hours on the water bath. To the cooled mixture was added 50 ml of 40% sodium hydroxide solution, the mixture extracted in the Soxhlet apparatus for 2 hours with ether, the ether extract dried over fused sodium hydroxide, the ether distilled through a dephlegmator, and the residue distilled. The yield of 3,3-dimethyl-2-propyl-(2)-pyrroline was 7.4 g (70%).

B.p. 157–158° (745 mm), n_D^{20} 1.4471, d_4^{20} 0.8340, MR_D 44.60; calc. 44.69.

This substance is an extremely volatile liquid with an acrid odor. Working with it causes headaches and smarting of the eyes. The picrate from anhydrous alcohol has m.p. 189° (decompn.).

Found %: C 49.00, 49.21; H 5.68, 5.58. $C_{15}H_{20}O_7N_4$. Calculated %: C 48.91; H 5.48.

The styphnate has m.p. 184° (precipitated from ether). The flavianate is a yellow-green oil, insoluble in anhydrous benzene and soluble in ether. The N-benzenesulfonamido derivative is an oil. The N-phenylureido derivative, m.p. 203° (from anhydrous alcohol).

Found %: N 10.82, 10.98. $C_{16}H_{22}ON_2$. Calculated %: N 10.85.

3,3-Dimethyl-2-phenylpyrroline. To a hypobromite solution, prepared from 4.38 g of sodium hydroxide, 35 ml of water and 1.5 ml of bromine, was added in small portions at room temperature 3.5 g of γ-methyl-γ-benzoylvaleramide. After the amide had completely dissolved the mixture was heated for 1 hour at a water bath temperature of 70-80°, cooled, extracted several times with ether, the extract dried over fused sodium hydroxide, and the ether distilled off. Vacuum-distillation of the residue gave 1.6 g (58%) of 3,3-dimethyl-2-phenylpyrroline, having a pleasant odor.

B.p. 119–121° (17 mm), n_D^{20} 1.5440, d_4^{20} 0.9983, MR_D 54.79; calc. 54.95.

Picrate, m.p. 160° (from anhydrous alcohol).

Found %: C 53.87, 53.78; H 4.49, 4.50. $C_{18}H_{18}O_7N_4$. Calculated %: C 53.72; H 4.51.

N-Phenylureido Derivative, m.p. 230° (sublimes in a sealed capillary).

Found %: N 9.63, 9.71. $C_{19}H_{20}ON_2$. Calculated %: N 9.58.

SUMMARY

1. A new method for the preparation of pyrrolines by the Hofmann rearrangement of δ-oxo amides has been described.

2. Two δ-oxo amides and two substituted pyrrolines have been described for the first time.

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MOLECULAR CHROMATOGRAPHY

III. SEPARATION OF MIXTURES OF NITROPHENOLS AND NITROPHENYLNITRAMINES

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In previous communications [1, 2] a method was proposed for the chromatographic separation of mixtures composed of one-type compounds and belonging to the class of aromatic acids, and specifically, the separation of mixtures of nitrophenols and mixtures of nitrophenylnitramines; here it was noted that a definite relationship between the acidity and the ability to be adsorbed is observed within the limits of these groups of compounds. In this respect it was of interest to study the mixtures composed of compounds of two different classes of aromatic acids. With this in mind the mixtures of nitrophenols and nitrophenylnitramines were studied.

For comparison of mixtures the following were taken: o-nitrophenol (I), m-nitrophenol (II), p-nitrophenol (III), 2,4-dinitrophenol (IV), o-nitrophenylnitramine (V), p-nitrophenylnitramine (VI) and 2,4-dinitrophenylnitramine (VII). Three mixtures were studied, with composition: 1) (III) + (VI); 2) (IV) + (VI) and 3) a mixture of all seven compounds.

Moist aluminum oxide was used as the adsorbent, while benzene, ether, or their mixtures, were used as solvents. The synthesis of the nitramines and the experimental procedure are given in previous communications [1, 2].

Experimentally it was shown that complete separation of the compounds can be achieved in all cases.

On the basis of the obtained data the studied nitrophenols and nitramines can be arranged in the following order of adsorption (in the order of increasing adsorbability):

(I) > (II) > (III) > (IV) > (VI) > (V) > (VII).

The earlier noted relationship existing between the acidity and the ability to be adsorbed is also observed for the mixtures that are composed of different types of compounds. In accord with their greater acidity all of the nitrophenylnitramines are found to be above any of the taken nitrophenols. The arrangement order of the compounds in the column is found to be in accord with the order of change in their dissociation constants (cf. Table).

TABLE

Names of the Compounds	Arrangement Order in the Column (From Lower to Higher)	Values of the Dissociation Constants
o-$C_6H_4(NO_2)OH$ (I)	1	$7.5 \cdot 10^{-8}$
m-$C_6H_4(NO_2)OH$ (II)	2	$1.0 \cdot 10^{-8}$
p-$C_6H_4(NO_2)OH$ (III)	3	$9.6 \cdot 10^{-8}$ 25° [3]
2,4-$C_6H_3(NO_2)_2OH$ (IV)	4	$1.0 \cdot 10^{-4}$
p-$C_6H_4(NO_2)NHNO_2$ (VI)	5	$1.12 \cdot 10^{-4}$
o-$C_6H_4(NO_2)NHNO_2$ (V)	6	$1.32 \cdot 10^{-3}$ 15 [4]
2,4-$C_6H_3(NO_2)_2NHNO_2$ (VII)	7	$8.86 \cdot 10^{-3}$*

* In view of the absence of literature data for (VII) the calculated value of the dissociation constant is presented (cf. [2]).

As can be seen from the table, the relationship existing between the order of adsorption and the acidity fails to be observed only in the case of o- and m-nitrophenol, which, possibly, is caused by the considerably greater solubility of (I) when compared to (II).

EXPERIMENTAL

The construction of the apparatus, the preparation of the moist aluminum oxide, the experimental procedure, and the method of extracting the adsorbed compounds from the adsorbent are all described in the paper on the separation of mixtures of nitrophenols [1]. The syntheses of the nitramines are described in the preceding communication [2]. All of the experiments were run under a slight pressure excess (20-100 mm) at room temperature.

1) p-Nitrophenol (III) and p-Nitrophenylnitramine (VI). A mixture of 0.10 g of (III) and 0.10 g of (VI) in 40 ml of benzene, column 154 x 14 mm, moisture content of aluminum oxide 14.2-14.3% (110-115°); elution – benzene 90 ml, pressure 40 mm. Two main zones (from bottom to top): diffuse, from yellow to greenish-yellow, width 76 mm (1st fraction), and greenish-yellow, 22 mm (2nd fraction). Isolated: 1st fraction - yellowish crystals, yield 0.06 g (60%), m.p. 114-114.3°; mixed melting point with p-nitrophenol (m.p. 113.5-114.5°) is 113.3-114°; 2nd fraction –light-yellow crystals, yield 0.09 g (90%), m.p. 112-112.5°; its mixture with p-nitrophenylnitramine (m.p. 112.5-113°) melts at 112.8-113°.

2) 2,4-Dinitrophenol (IV) and p-Nitrophenylnitramine (VI). A mixture of 0.10 g of (IV) and 0.10 g of (VI) in 50 ml of benzene, column and adsorbent the same as in the preceding experiment; elution - benzene 130 ml, pressure 20 mm. Two main zones (from bottom to top): bright-yellow, width 34 mm (1st fraction), and greenish-yellow, 22 mm (2nd fraction), separated by a narrow colorless zone.

Isolated: 1st fraction - light-yellow plates and scales, yield 0.06 g (60%), m.p. 114-114.9°; its mixture with 2,4-dinitrophenol (m.p. 113.5-114°) melts at 113.5-114°; 2nd fraction – light-yellow crystals, yield 0.07 g (70%), m.p. 113.5-114°; its mixture with p-nitrophenylnitramine (m.p. 112.5-113°) melts at 113.5-114°.

3) o-Nitrophenol (I), m-Nitrophenol (II), p-Nitrophenol (III), 2,4-Dinitrophenol (IV), o-Nitrophenylnitramine (V), p-Nitrophenylnitramine (VI) and 2,4-Dinitrophenylnitramine (VII).

A mixture of 0.10 g of each of the indicated compounds in 50 ml of benzene, column 495 x 14 mm, moisture content of aluminum oxide 15.5% (110-115°); elution – benzene 150 ml, benzene-ether mixture (100:1) 50 ml, (100:3) 25 ml, (1:1) 50 ml, ether 200 ml; pressure 70-100 mm. After washing the column with benzene and the benzene-ether mixtures, some of the zones were eluted into the filtrate. The filtrate fractions were collected (in order of removal), light-yellow from the light-yellow zone, width 325 mm * (1st fraction), pale yellow from the light-yellow zone, width 260 mm (2nd fraction), and light-yellow from the greenish-yellow zone, width 190 mm (3rd fraction). After washing with ether four zones with fixed boundaries are found in the column (from bottom to top): bright-yellow 40 mm (4th fraction), greenish-yellow, 25 mm (5th fraction), narrow white intermediate, light greenish-yellow, 40 mm (6th fraction), narrow white intermediate, and bright greenish-yellow, 11 mm (7th fraction). In the usual manner there was isolated: 1st fraction – yellow crystals, yield 0.06 g (60%), m.p. 45.5-46°; its mixture with o-nitrophenol (m.p. 44.7-45.5°) melts at 45-45.5°; 2nd fraction – pale yellow crystals, yield 0.08 g (80%), m.p. 96.3-97°; its mixture with m-nitrophenol (m.p. 97.2-97.7°) melts at 97.3-97.7°; 3rd fraction – light-yellow crystals, yield 0.09 g (90%), m.p. 114.7-115.4°; its mixture with p-nitrophenol (m.p. 113.5-114.5°) melts at 114-114.3°; 4th fraction – yellow crystals, yield 0.10 g (100%), m.p. 82.5-92.3°; chromatographically purified on the same adsorbent from benzene; isolated 0.08 g (80%), m.p. 114.3-114.6°; its mixture with 2,4-dinitrophenol (m.p. 113.5-114°) melts at 114-114.3°; and 0.02 g (20%), m.p. 113.5-114°; its mixture with p-nitrophenylnitramine (m.p. 112.5-113°) melts at 113.2-113.8°; 5th fraction – light-yellow crystals, yield 0.06 g (60%), m.p. 98-104.5°; chromatographically purified on the same adsorbent from benzene; isolated 0.05 g (50%), m.p. 112-112.5°; its mixture with p-nitrophenylnitramine melts at 112.7-113.2°; 6th fraction– light yellow crystals, yield 0.08 g (80%), m.p. 64.5-66°; its mixture with o-nitrophenylnitramine (m.p. 66.5-67.5°) melts at 66-67.5°; 7th fraction – light yellow crystals, yield 0.09 g (90%), m.p. 58-68°; purified twice on the same adsorbent from benzene and ether; isolated 0.06 g (60%) of light-yellow plates with m.p. 102.5-103.5°; its mixture with 2,4-dinitrophenylnitramine (m.p. 103.3-104°) melts at 102.5-103.5°.

SUMMARY

1. Several mixtures, consisting of nitrophenols and nitrophenylnitramines (o-, m- and p-nitrophenols, 2,4-dinitrophenol, o- and p-nitrophenylnitramines, and 2,4-dinitrophenylnitramine), were chromatographically separated from benzene and ether on moist aluminum oxide.

* The width of the zone was measured at the moment when the zone began to be eluted into the filtrate.

2. It was found that the relationship shown to exist between the ability to be adsorbed and the acidity for mixtures of nitrophenols is also observed for mixtures that contain different types of compounds, namely, the nitrophenols and the nitrophenylnitramines.

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• T. p. = C. B. Translation pagination.

REACTION OF ALCOHOL OXIDES OF THE ACETYLENE SERIES WITH HYDROGEN SULFIDE

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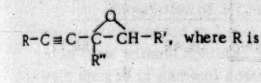
In previous researches it was established by one of us that the reaction of hydrogen sulfide with the oxides and alcohol oxides of acetylenes and vinylacetylenes of the type:



$R-C\equiv C-\underset{R''}{\overset{O}{\underset{|}{\overset{|}{C}}}}-CH-R'$, where R is vinyl, alkyl, etc., leads to the formation of the corresponding thiophene homologs [1].

The purpose of the present study was to obtain some hydroxy derivatives of thiophene. This investigation was of interest for the reason that such compounds have not been described in the literature and a one-step method for their preparation was not known. In addition, it was of theoretical interest to determine the possibility of dehydrating the hydroxy derivatives of thiophene, obtaining the corresponding cyclohexenyl- and cyclopentenylthiophenes.

The following oxides were taken for study: 2-methyl-4-(1-hydroxycyclohexyl)-1,2-oxido-3-butyne (I) and 2-methyl-4-(1-hydroxycyclopentyl)-1,2-oxido-3-butyne (II), which were obtained by the action of powdered potassium hydroxide in anhydrous ether on the corresponding hydroxychlorohydrins – 1-chloro-2-methyl-4-(1-hydroxycyclohexyl)-3-butyn-2-ol (III), 1-chloro-2-methyl-4-(1-hydroxycyclopentyl)-3-butyn-2-ol (IV).

The reaction of the alcohol oxide (I) with hydrogen sulfide gave dark-rose crystals, having the composition $C_{11}H_{16}OS$. The Reinboldt test for the mercapto group was negative. The percent of active hydrogen corresponded to the presence of one hydroxyl group. With mercuric acetate the substance gave a flocculent precipitate, which melted with decomposition, and with isatin sulfate it gave a dark-purple coloration. When dehydrated with 5% sulfuric acid this substance gave a compound with the empirical formula $C_{11}H_{14}S$, a liquid that shows qualitative reactions for thiophene. Its mercury derivative, a white flocculent precipitate, melted with decomposition.

On the basis of earlier syntheses of thiophene homologs by the same method [2], the elementary analysis, and the qualitative tests for the thiophene nucleus, the synthesized compound can be assigned the structure: 4-methyl-2-(1-hydroxycyclohexyl)-thiophene (V), and to its dehydration product the structure 4-methyl-2-(1-cyclohexenyl)thiophene (VI).

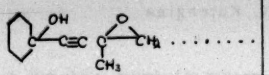
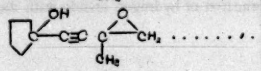
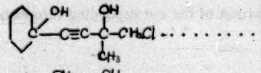
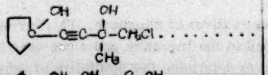
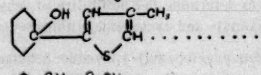
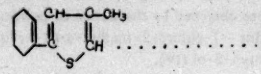
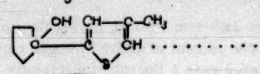
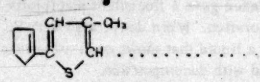
The reaction product of 2-methyl-4-(1-hydroxycyclopentyl)-1,2-oxido-3-butyne (II) with hydrogen sulfide proved to be a liquid of low mobility and having the composition $C_{10}H_{14}OS$, which also failed to give a qualitative test for the mercapto group. The active hydrogen content corresponded to one hydroxyl group. Water was spontaneously lost when the substance was stored. The qualitative reactions for the thiophene nucleus were positive. When dehydrated with 5% sulfuric acid the compound of composition $C_{10}H_{12}S$ was obtained in good yield. The latter compound is a fairly mobile liquid and gives positive qualitative reactions for thiophene. The mercury derivative, a white flocculent precipitate, decomposes at 151°. On the basis of the obtained data the synthesized compounds can be assigned the structures: 4-methyl-2-(1-hydroxycyclopentyl)-thiophene (VII) and 4-methyl-2-(cyclopentyl)thiophene (VIII). The compound with the five membered ring is less stable than the thiophene homolog with the six-membered ring.

The reaction of alcohol oxides with hydrogen sulfide is accompanied by heat evolution and is practically ended in 30 minutes. The formulas and physical constants of all of the prepared compounds are given in the Table.

EXPERIMENTAL

1. Preparation of 1-Chloro-2-methyl-4-(1-hydroxycyclohexyl)-3-butyn-2-ol (III). In a round-bottomed flask, fitted with mechanical stirrer, dropping funnel and reflux condenser, was placed 12 g of magnesium and 100 ml of anhydrous ether, and gradually an ether solution of ethyl bromide was added. To the obtained Grignard reagent solution the ethynylcyclohexanol (in ether) was slowly added in drops. Then the flask was heated (35-36°) for 1 hour with constant stirring, and to the mixture was added 45 g of chloroacetone. The organomagnesium complex was decomposed with 30% acetic acid. The obtained substance was extracted with ether. The ether extract was dried over fused $MgSO_4$. After removal of the ether and as the result of two distillations the residual substance was separated into two fractions: First-unreacted carbinol, 5 g, and second- with b.p. 129-130° at 2 mm, 12 g.

TABLE

Compound No.,	Formula	Boiling point at pressure (mm)	n_D^{20}	d_4^{20}	MR_D Calculated	MR_D Found
I		101–102 (1.5)	1.4965	1.0429	50.21	50.36
II		96–98 (1)	1.4940	1.0463	45.28	46.24
III		129–130 (2)	1.5210	1.1690	56.42	56.71
IV		with decomposition at 90° (2)	–	–	–	–
V		124–126 (2) m.p. 52–53°	–	–	–	–
VI		105–106 (3)	1.5790	1.0580	55.12	55.97
VII		105–106 (2)	1.5434	1.1010	52.61	52.14
VIII		76–77 (0.5)	1.5765	1.0550	50.50	51.68

Found %: active H 0.548, 0.467; Cl 16.51, 16.69. $C_{11}H_{17}O_2Cl$. Calculated %: active H 0.463; Cl 16.38.

1-Chloro-2-methyl-4-(1-hydroxycyclohexyl)-3-butyn-2-ol is a greenish liquid of low mobility, and which distills in vacuo with partial decomposition. It gradually darkens when stored in the air. The yield of the product depends on the amount of solvent and the time of heating the reaction mixture in the preparation of the Iotisch reagent. An increase in both the amount of solvent and the time of heating increases the yield of the product to 70%.

2. Preparation of 2-Methyl-4-(1-hydroxycyclohexyl)-1,2-oxido-3-butyne (I). In a round-bottomed flask with reflux condenser and outlet tube was placed an ether solution of 50 g of the glycol chlorohydrin (III). To it in small portions was gradually added 50 g of powdered potassium hydroxide. After all of the alkali had been added the mixture was transferred to a separatory funnel. The alkali was dissolved in water and the aqueous layer was extracted with ether. The ether extract was dried over fused Na_2SO_4. The ether was distilled off on the water bath. The residue was fractionated in vacuo. As a result the oxide (I) was isolated, which crustallized on standing. Needle-like crystals of light-green color. Yield of oxide 32 g (80%).

Found %: active H 0.464, 0.569; C 73.24, 73.26; H 9.45, 9.57. $C_{11}H_{16}O_2$. Calculated %: active H 0.569; C 73.33; H 9.42.

3. Preparation of 4-Methyl-2-(1-hydroxycyclohexyl)thiophene (V). To 150 ml of water and 20 g of barium hydroxide, contained in a round-bottomed flask with mechanical stirrer and reflux condenser, was added 32 g of the oxide (I). With constant stirring a stream of hydrogen sulfide was passed into the reaction flask. The temperature of the mixture spontaneously rose to 50°. After adding all of the oxide the passage of hydrogen sulfide was continued for another half hour. Then the calculated amount of acetic acid was added to the reaction flask. The obtained substance was extracted with ether. The ether extract was dried over potash. After distilling off the ether the dark-rose crystalline residue was vacuum-distilled. The crystals, purified by distillation, melted at 52-53°. Yield of substance 34 g (91%).

Found %: active H 0.550, 0.552; S 16.59, 16.30. $C_{11}H_{16}OS$. Calculated %: active H 0.547; S 16.36.

The obtained compound gives the characteristic purple coloration with isatin sulfate. With mercuric acetate it forms a white flocculent precipitate, which melts with decomposition.

4. Preparation of 4-Methyl-2-(1-cyclohexenyl)thiophene (VI). In a one liter Wurtz flask was placed 400 ml of 5% sulfuric acid and 32 g of substance (V). The mixture was steam-distilled under constant volume. The distillate was extracted with ether. The ether extract was dried over fused Na_2SO_4. After distilling off the ether the isolated substance was fractionated in vacuo.

Found %: S 17.51, 17.69. $C_{11}H_{14}S$. Calculated %: S 17.99.

5. Preparation of 1-Chloro-2-methyl-4-(1-hydroxycyclopentyl)-3-butyn-2-ol (IV). The ethynylcyclopentanol was gradually added to 1 mole of the Grignard reagent dissolved in 600 ml of anhydrous ether. The carbinol was added in drops without cooling. During the carbinol addition the mixture thickened and became light-gray in color. Toward the end of carbinol addition the mixture stratified, the bottom layer being a light-gray mass and the top being a nearly transparent ether layer. After all of the carbinol had been added the stirring was continued for 45 minutes with heating. In measure with chloroacetone addition (30 g) the deposit darkened and partly dissolved. After all of the chloroacetone had been added the stirring was continued for 3 hours with heating. The organomagnesium complex was treated in the usual manner. We were unable to isolate the pure glycol chlorohydrin since it underwent decomposition when vacuum-distilled; consequently, the oxide (II) was obtained from the impure product.

6. Preparation of 2-Methyl-4-(1-hydroxycyclopentyl)-1,2-oxido-3-butyne (II). The oxide was synthesized the same as above by treating an ether solution of the glycol chlorohydrin with powdered potassium hydroxide. The yield of oxide was 20 g (35%).

Found %: C 72.19, 72.17; H 8.51, 8.55; active H 0.592, 0.610. $C_{10}H_{14}O_2$. Calculated %: C 72.26; H 8.48; active H 0.606.

7. Preparation of 4-Methyl-2-(1-hydroxycyclopentyl)thiophene (VII). Synthesized in the same way as 4-methyl-2-(1-hydroxycyclohexyl)thiophene (V). For reaction was taken 20 g of barium hydroxide, 150 ml of water and 16 g of the oxide. The yield of substance was 9 g (51%).

Found %: active H 0.549, 0.546; S 17.34, 17.26. $C_{10}H_{14}SO$. Calculated %: active H 0.553; S 17.59.

The obtained compound gives the characteristic purple color with isatin sulfate. With mercuric acetate a white crystalline substance is obtained, which melts with decomposition.

8. Preparation of 4-Methyl-2-(1-cyclopentyl)thiophene (VIII). The treatment of 7.6 g of (VII) with 5% sulfuric acid gave 5 g of 4-methyl-2-(1-cyclopentenyl)thiophene (73.1%).

Found %: S 19.36, 19.32. $C_{10}H_{12}S$. Calculated %: S 19.52.

Qualitative reaction with isatin sulfate gave a bright-purple color. The mercury derivative melts at 151° (with decompn.).

SUMMARY

1. The new chlorohydrins were synthesized by the Grignard-Iotsich method: 1-chloro-2-methyl-4-(1-hydroxycyclohexyl)-3-butyn-2-ol (III) and 1-chloro-2-methyl-4-(1-hydroxycyclopentyl)-3-butyn-2-ol (IV).

2. Treatment of the chlorohydrins (III) and (IV) in anhydrous ether with powdered potassium hydroxide gave the previously unknown oxides: 2-methyl-4-(1-hydroxycyclohexyl)-1,2-oxido-3-butyne (I) and 2-methyl-4-(1-hydroxycyclopentyl)-1,2-oxido-3-butyne (II).

3. Treatment of the oxides, containing either a five-membered or a six-membered ring as substituent for the acetylenic hydrogen, with hydrogen sulfide in alkaline medium made it possible to realize the one-step synthesis of: 4-methyl-2-(1-hydroxycyclohexyl)-thiophene (V) and 4-methyl-2-(1-hydroxycyclopentyl)thiophene (VI).

4. The dehydration of the hydroxythiophene homologs gave: 4-methyl-2-(1-cyclohexenyl)thiophene (VII) and 4-methyl-2-(1-cyclopentenyl)thiophene (VIII).

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CONTACT CATALYZED TRANSFORMATION OF TETRAHYDROSILVAN INTO CYCLOPENTADIENE

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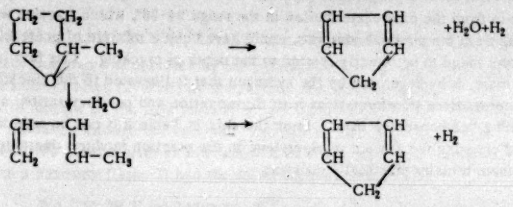
Among the catalytic transformations of tetrahydrosilvan (2-methyltetrahydrofuran) a number of authors investigated its dehydration for the purpose of obtaining piperylene (1,3-pentadiene). Thus, de Melle and Guinot [1] ran the reaction for the dehydration of tetrahydrosilvan into piperylene over aluminum phosphate at 350°. Burnette [2] used aluminum oxide as the dehydration catalyst. It was found by him that the yield of piperylene varied from 17% at atmospheric pressure to 30% at 70 mm of mercury pressure. The greatest yield of piperylene (91%) was obtained by the dehydration of tetrahydrosilvan at 350° over a catalyst composed of equal amounts of boric and phosphoric acids [3]. On the other hand, it was established [4] that at 600-620° and reduced pressure a certain amount of cyclopentadiene is formed from piperylene; consequently, it was of interest to elucidate the possibility of directly transforming tetrahydrosilvan into cyclopentadiene under the conditions where piperylene cyclization could occur.

The formation of cyclopentadiene from tetrahydrosilvan can be depicted as being the result of either simultaneous or sequential dehydration and dehydrogenation, proceeding in accord with Equations (1) or (2):



From thermodynamic data [5-7] we calculated the relationship between the logarithm of the equilibrium constant and the temperature for the formation of cyclopentadiene and piperylene from tetrahydrosilvan, and also for the transformation of piperylene into cyclopentadiene (Fig. 1). The values of the free energies of formation for cyclopentadiene at various temperatures was estimated from the known values of ΔZ for cyclopentane cyclopentene, proceeding from the assumption that:

$$\Delta Z_{\text{cyclopentadiene}} = 2\Delta Z_{\text{cyclopentene}} - \Delta Z_{\text{cyclopentane}}.$$

For tetrahydrosilvan the values of the free energies of formation were determined by adding the free energies of formation for tetrahydrofuran and the averaged values for the CH_2 group.

As is seen from Fig. 1. for a wide temperature range tetrahydrosilvan should for all practical purposes be completely converted into cyclopentadiene and piperylene. In addition, thermodynamically the formation of cyclopentadiene from tetrahydrosilvan should be realized more easily than from piperylene. However, by means of preliminary experiments on the dehydration of tetrahydrosilvan in contact with aluminum oxide at 300, 400 and 450° it was established that only at 400° is cyclopentadiene found in the reaction products, and here only in a total amount of about 1%. This circumstance caused us to run the dehydration of tetrahydrosilvan at higher temperatures (550 and 600°) and to study here the influence of various catalysts. We studied the catalytic activity of titanium oxide-aluminum oxide mixtures containing 5, 10 and 25 mole % of aluminum oxide, thorium-titanium, manganese-alumina catalysts, and zinc silicate (Zn_2SiO_4). The greatest yield of cyclopentadiene (20%) was obtained in the experiments with TiO_2 + Al_2O_3 (5% mol. Al_2O_3). To answer the question as to which equation – (1) or (2) – is obeyed in the formation of cyclopentadiene we studied, on the one hand, the behavior of piperylene under the same conditions as the transformation of tetrahydrosilvan was studied, and on the other hand, the relationship existing between the degree of tetrahydrosilvan transformation into cyclopentadiene and piperylene and the contact time. It was established by us that when the experiments are run under the same conditions the yields of cyclopentadiene are lower from piperylene than they are

from tetrahydrosilvan, and that cyclopentadiene and piperylene are formed from tetrahydrosilvan as the result of concurrent reactions. In turn, cyclopentadiene and piperylene suffer further transformations, as a result of which the curves for their formation rates assume a complex character.

The transformation of tetrahydrosilvan into cyclopentadiene in the presence of catalysts is a new reaction, the further study of which can be of considerable theoretical and practical interest. Our results show that the process for the formation of cyclopentadiene and piperylene from tetrahydrosilvan represents two independently parallel reactions.

In Fig. 2 are plotted the yields of cyclopentadiene (Curve 1) and of piperylene (Curve 2) as functions of the values for the reciprocal of the tetrahydrosilvan space flow rate ($\frac{1}{v}$) (the curves were constructed from the data given in Table 4).

As can be seen from Fig. 2, Curve 2 is bent around Curve 1 for all of the transformation intervals. This means that the rate for the formation of piperylene from tetrahydrosilvan is higher than is the rate for the formation of cyclopentadiene. From this figure it can also be seen that the curves for the formation of cyclopentadiene and of piperylene pass through a maximum. This shows that piperylene and cyclopentadiene suffer further transformations, evidently, in several directions, of which the greatest significance may be possessed by the reactions of hydrogen redistribution, cracking and polymerization. For the hydrogenation of piperylene

$$CH_2=CHCH=\overset{1}{C}HCH_3+H_2 \rightleftarrows \begin{matrix} CH_2=CHCH_2CH_2CH_3 \\ CH_3CH=CHCH_2CH_3 \end{matrix}$$

the equilibrium, in the investigated temperature interval, should be shifted to the right. Actually, the head fraction isolated by us from the catalyzates boiled in the range 24-39°, which fraction was not studied in datail, but which, judging from the physical constants, could have been a mixture of pentenes and pentane. The yields of this fraction were found to be directly related to the depth of cracking. This fact indicates that the formed piperylene, in the main, is hydrogenated by the hydrogen that is liberated in the cracking process. The main direction of further cyclopentadiene transformations is its dimerization and polymerization, as a result of which the catalyst is covered with a "carbonaceous film". From the data in Table 3 it can be seen that together with increase in the depth of cracking the amount of piperylene in the reaction products decreases, while the amount of cyclopentadiene in them remains practically constant.

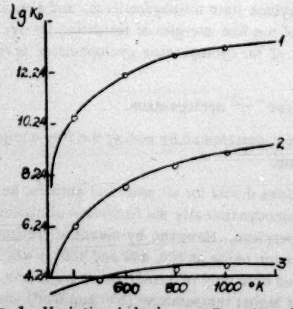


Fig. 1. Variation in $\log k_p$ as a Function of Reaction Temperature. 1) Tetrahydrosilvan → cyclopentadiene $+H_2O + H_2$, 2) tetrahydrosilvan → piperylene + H_2O, 3) piperylene → cyclopentadiene + H_2.

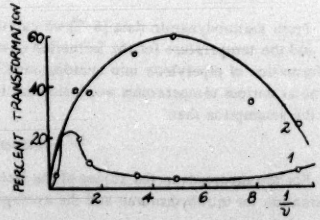


Fig. 2. Variation in the Yields of Hydrocarbons as a Function of the Reciprocal Volumetric Rate Values, in Contact with $TiO_2 + Al_2O_3$ (5 mole %) at 600°. 1) Cyclopentadiene, 2) piperylene.

As a result, under the investigated conditions for the contact catalyzed transformations of tetrahydrosilvan an extremely complex chain of parallel and sequential reactions is observed.

From the positions of the maxima on the curves for the formation of cyclopentadiene and piperylene from tetrahydrosilvan a comparison can be made of the relationship existing between the constant for the formation of cyclopentadiene and its further transformations and the relationship existing between the constant for the formation of piperylene and its subsequent transformation into other products. Since the maximum for the accumulation of cyclopentadiene in the reaction products

lies at the very beginning of reaction, then it is evident that the velocity constant for its formation k_1 will be considerably higher than the velocity constant for its further transformation k_1'. And since the maximum for the accumulation of piperylene on the formation curve lies to the right of the maximum for the formation of cyclopentadiene, then $\frac{k_1}{k_1'} > \frac{k_2}{k_2'}$, where k_2 is the velocity constant for the formation of piperylene, and k_2' is the velocity constant for its further transformations; consequently, with increase in the contact time a gradual increase in the amount of cyclopentadiene in the reaction products can be expected as the result of its additional formation from piperylene, which was confirmed experimentally (Table 4). Comparative experiments on the transformations of tetrahydrosilvan and piperylene under similar conditions (Table 5) show that cyclopentadiene is formed in greater amount from tetrahydrosilvan than it is from piperylene. These results, and also the data in Table 4, lead to the conclusion that cyclopentadiene, within quite wide limits for the time of contact of tetrahydrosilvan with the catalyst, is formed directly from it (tetrahydrosilvan) as the result of dehydration and dehydrogenation reactions, simultaneously proceeding on the catalyst surface. Of all of the catalysts investigated by us the most active for the conversion of tetrahydrosilvan into cyclopentadiene proved to be the titanium oxide-alumina catalysts. An increase in the amount of aluminum oxide in these catalysts considerably increased the cracking action of the catalyst without essentially changing its capacity to effect the transformation of tetrahydrosilvan into cyclopentadiene. Of interest is the fact that the manganese-alumina catalyst, containing a large amount of aluminum oxide when compared with the titanium oxide-alumina catalysts, exhibits extremely insignificant cracking properties.

On zinc silicate the tetrahydrosilvan at 600° underwent hardly any changes. This circumstance indicates the high thermal stability of tetrahydrosilvan.

EXPERIMENTAL

Synthesis of Starting Substances and Preparation of Catalysts

Tetrahydrosilvan was obtained by the hydrogenation of silvan (2-methylfuran) on skeletal nickel catalyst, prepared from a Ni-Al alloy (27% Ni) by the method previously described by one of us [8]. The hydrogenation was run in an electric furnace by the flow method at 125° and a space velocity of 0.06 hr.$^{-1}$ in excess hydrogen with a single pass of the substance through the catalyst. The tetrahydrosilvan was isolated from the hydrogenation products by distillation through a column with an efficiency of 70 theoretical plates and was distilled a second time over metallic sodium from a Favorsky flask; it had the following constants:

B.p. 79–79.2° (at 745 mm); d_4^{20} 0.8582, n_D^{20} 1.4087. From literature [9] tetrahydrosilvan has b.p. 78.5–80° (at 746 mm), d_4^{20} 0.8552 and n_D^{20} 1.4072.

Piperylene was isolated from the technical product by fractionation through a column with an efficiency of 70 theoretical plates and had b.p. 41.7-43.8° (at 757 mm); it had d_4^{20} 0.6834 and n_D^{20} 1.4317 and was a mixture of the cis- and trans-forms.

Literature [10] for trans-piperylene: B.p. 41.7 (at 745 mm), d_{20}^{20} 0.6771 and n_D^{20} 1.4300; for cis-piperylene: B.p. 43.8 (750 mm), d_{20}^{20} 0.6916 and n_D^{20} 1.4360.

The Manganese-Alumina Catalyst with a Content of 33 Mole % Al_2O_3 and 67 Mole % MnO was prepared by the joint precipitation with 25% aqueous ammonia of aluminum and manganese hydroxides from a combined solution of manganese and aluminum nitrates. After washing free of nitrate ion (reaction with diphenylamine) the precipitate was filtered, molded into small 3-4 mm cylinders, dried at 150°, and prior to use was reduced in the reaction tube with hydrogen until water ceased to be evolved when the temperature was gradually raised from 300 to 600°.

The Specimens of Titanium-Alumina Catalyst with an aluminum oxide content of 5, 10 and 25 mole % were obtained by the thorough mixing (grinding in a mortar) of pure titanium dioxide and freshly precipitated aluminum hydroxide. The catalyst was molded into pellets, which were dried at 150°.

Zinc Silicate was prepared by mixing freshly precipitated zinc hydroxide (2 moles) and silica gel, obtained by the coagulation of a solution containing 1 mole of sodium silicate with 0.1 N hydrochloric acid, followed by washing to remove Cl-ion. The catalyst was molded into cylindrical pellets and dried at 150°.

The Thorium-Titanium Catalyst, containing 25 mole % of thorium dioxide, was prepared by thoroughly mixing the pure titanium and thorium oxides.

Catalytic Transformations of Tetrahydrosilvan

The catalytic transformations of tetrahydrosilvan were studied in a quartz tube of length 120 cm and internal diameter of 16 mm by the flow method under reduced pressure. In the tube was placed 100 ml of catalyst. The vacuum used in the different experiments ranged from 18 to 60 mm of mercury pressure. The temperature was measured with a chromel-alumel thermocouple with an accuracy of ± 5°. Each experiment was run with either 50 g of tetrahydrosilvan or piperylene. The experiments involving kinetic measurements were run with 15 g portions of tetrahydrosilvan.

TABLE 1

Transformations of Tetrahydrosilvan in Contact with Al_2O_3

Expt. No.	Experimental Conditions		Yield of Liquid Catalyzate (in %)	Yield of Dienes (in % of the Theoretical)	
	Pressure (in mm)	Temperature		Cyclopentadiene	Piperylene
1	750	300°	73.0	Absent	1.9
2	18–20	400	70.0	0.8	12.1
3	745	450	43.5	Absent	Traces
4	55–60	450	76.0	1.9	10.6

TABLE 2

Transformations of Tetrahydrosilvan in Contact with Al_2O_3 + MnO (1:2), TiO_2 + ThO_2 (3:1) and Zn_2SiO_4

Expt. No.	Catalyst	Experimental Conditions		Yield of Liquid Catalyzate (in %)	Amount of Unchanged Tetrahydrosilvan (in %)	Yield of Dienes (in % of the Theoretical)	
		Pressure (in mm)	Temperature			Cyclopentadiene	Piperylene
1	Al_2O_3 + MnO	20–25	550°	97	70	0.6	14.8
2	Al_2O_3 + MnO	20–25	600	95	66	1	17.3
3	TiO_2 + ThO_2	50	600	90	0	3.2	Not investigated
4	Zn_2SiO_4	30	600	98	96	Traces	Traces

TABLE 3

Transformations of Tetrahydrosilvan in Contact with TiO_2 + Al_2O_3

Expt. No.	Amount of Al_2O_3 in Catalyst (in Mole %)	Experimental Conditions		Yield of Liquid Catalyzate (in %)	Yield of Dienes (in % of the Theoretical	
		Pressure (in mm)	Temperature		Cyclopentadiene	Piperylene
1	5	30–35	600°	92	5.4	34.7
2	10	30–40	600	70	4.6	28.5
3	25	30–45	600	34	4.5	18.8

TABLE 4

Variation in the Yields of Cyclopentadiene and Piperylene as a Function of the Space Velocity for the Passage of Tetrahydrosilvan over TiO_2 + Al_2O_3 (5%) at 600° and 25–30 mm

Expt. No.	Space Velocity (in Hr.$^{-1}$)	Yield of Dienes (in % of the Theoretical)	
		Cyclopentadiene	Piperylene
1	5	5.1	Not investigated
2	1	20.0	39.7
3	0.7	9.4	36.3
4	0.3	4.6	52.3
5	0.2	3.6	59.3
6	0.1	6.5	25.1

The starting substance was fed into the reaction zone from an automatic burette at a space velocity of 0.2 hr.$^{-1}$. The reaction products were first collected in a receiver, cooled with water, and then in three traps connected in series, of which the first two were immersed in a dry ice-methyl alcohol mixture, while the last one was immersed in liquid nitrogen. The depth of partial cracking was judged by the yield of liquid catalyzate. The amount of cyclopentadiene in the catalyzate was determined immediately after termination

TABLE 5

Yield of Cyclopentadiene in the Transformations of Tetrahydrosilvan and Piperylene in Contact with TiO_2 + + Al_2O_3 (5%), TiO_2 + Al_2O_3 (9 : 1)

Expt. No.	Catalyst	Experimental Conditions		Substance Transformed	Space Velocity (in Hr.$^{-1}$)	Amount of Cyclopentadiene (in % of the Theoretical)
		Pressure (in mm)	Temperature			
1	TiO_2 + Al_2O_3 (5%)	30–35	600°	Tetrahydrosilvan	0,5	6,2
				Piperylene	0,5	2,0
2	TiO_2 + Al_2O_3 (9:1)	30–40	600	Tetrahydrosilvan	0,2	4,6
				Piperylene	0,2	2,9

of the experiment by the colorimetric method proposed by Afanasyev [11]. The total amount of dienes was established by the method of Krause, Kogan and Polievktova [12], involving the preparation of the maleic anhydride adduct. The yield of piperylene was calculated by difference between the total amount of dienes and the amount of cyclopentadiene. The catalyzate was distilled through a column with an efficiency of 30 theoretical plates. The experimental results are given in Tables 1-5.

SUMMARY

1. It was shown that cyclopentadiene (in yields up to 20%) and piperylene (in yields up to 60%) are formed in the contact transformations of tetrahydrosilvan on different oxide catalysts at 550-600° under reduced pressure.

2. It was established that the formation of both cyclopentadiene and of piperylene from tetrahydrosilvan occurs as the result of concurrent reactions. Under these conditions a part of the cyclopentadiene can also be obtained from the piperylene.

3. The action of a number of catalysts (titanium-alumina and others) in the reactions for the formation of cyclopentadiene and piperylene from tetrahydrosilvan was studied.

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POSTULATED REACTIONS FOR THE PHOTOSYNTHESIS OF GLYCINE, SERINE AND PROLINE IN A MIXTURE OF PARAFORMALDEHYDE AND POTASSIUM NITRATE

Krishna Bakhadur and S. Ranganayaki

It was shown earlier [1] that a number of amino acids are formed when a mixture of paraformaldehyde, potassium nitrate, ferric chloride and water is exposed to the action of light. Together with other amino acids, glycine, serine and proline are formed in the mixture. In this communication we present a hypothetical scheme for the reactions leading to the formation of these amino acids.

The nitrate is reduced by the paraformaldehyde to ammonia In the form of ammonia the nitrogen is utilized for the synthesis of amino acids. In the formation of glycine, serine and proline the light probably activates the molecules of the above described mixture in such a manner that the reactions of hydration, hydrogenation and dehydrogenation become possible. These types of reactions have long been known in the processes for the synthesis of various organic compounds in plants. Below we present our postulated reactions for the formation of glycine, serine and proline.

Most of these reactions are also possible of achievement under laboratory conditions.

$$2CH_2O + H_2O \rightleftharpoons CH_3OH + HCOOH \quad (1)$$

$$CH_2O + HCOOH \rightleftharpoons HOCH_2COOH \quad (2)$$

$$HOCH_2COOH \rightleftharpoons CHOCOOH + 2H \quad (3)$$

$$CHOCOOH + 2NH_3 \rightleftharpoons NH_2CH(OH)COONH_4 \quad (4)$$

$$NH_2CH(OH)COONH_4 + H_2O \rightleftharpoons NH_2CH(OH)COOH + NH_4OH \quad (5)$$

$$NH_2CH(OH)COOH \rightleftharpoons NH = CHCOOH + H_2O \quad (6)$$

$$NH = CHCOOH + 2H \rightleftharpoons NH_2CH_2COOH \text{ (glycine)} \quad (7)$$

$$NH = CHCOOH + CH_2O \rightleftharpoons CHOCH(NH_2)COOH \quad (8)$$

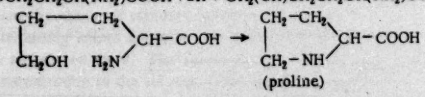
$$CHOCH(NH_2)COOH + 2H \rightleftharpoons CH_2(OH)CH(NH_2)COOH \text{ (serine)} \quad (9)$$

$$CH_2O + CH_2(OH)CH(NH_2)COOH \rightleftharpoons CHOCH_2CH(NH_2)COOH + H_2O \quad (10)$$

$$CHOCH_2CH(NH_2)COOH + 2H \rightleftharpoons HOCH_2CH_2CH(NH_2)COOH \quad (11)$$

$$CH_2O + HOCH_2CH_2CH(NH_2)COOH \rightleftharpoons CHOCH_2CH_2CH(NH_2)COOH + H_2O \quad (12)$$

$$CHOCH_2CH_2CH(NH_2)COOH + 2H \rightleftharpoons CH_2(OH)CH_2CH_2CH(NH_2)COOH \quad (13)$$



(proline) (14)

In studying the formation of amino acids in Torulopsis utilis it was found that glycine is transformed into serine and proline [2]. This is analogous to the reactions shown in the above presented scheme. It was also observed by Stekol and coworkers [3, 4], and by Arnstein and Neuberger [5, 6], that in living tissues glycine is utilized for the synthesis of serine in the presence of vitamin B_{12}. The formation of serine from glycine was also observed by Sakami [7], who showed that when rats were fed C^{14} -labeled formic acid and glycine, C^{13} -labeled in the carboxyl group ($CH_2NH_2C^{13}OOH$), that the serine which was isolated from the liver proteins also proved to be labeled in similar fashion; $C^{14}H_2(OH)CH(NH_2)C^{13}OOH$. Here the postulated reaction was: $HC^{14}OOH + CH_2(NH_2)C^{13}OOH \rightarrow C_{14}H_2(OH)$-$CH(NH_2)C^{13}OOH$.

If here the formic acid is converted in the liver to CH_2O, then the reaction would be in exact agreement with the above postulated scheme.

The interrelationships existing between glycine, serine and proline are also supported by the studies made on the Torulopsis utilis yeasts. These yeasts are capable of converting alanine, labeled with C^{13} in the carboxyl group,

into serine and proline. The fact that the formation of glycine from serine is a reversible process [8] also supports the possibility of interconversions for these compounds.

As a result, it seems to us that the above presented process for the conversion of glycine into serine, and then into proline, is found in complete agreement with the results of the observations made on the biochemical syntheses of these amino acids. The solitary difference in the synthesis of these amino acids under laboratory conditions in the light and their synthesis in living tissues is the fact that in the latter case the enzymes and vitamins cofunction to complete the synthesis, while in the first case these reactions proceed as the result of activation of the molecules by the action of sunlight.

SUMMARY

It was established that a number of amino acids are formed when a mixture of paraformaldehyde, potassium nitrate, ferric chloride and water is exposed to the action of sunlight.

A hypothetical scheme is presented for the reactions leading to the formation of glycine, serine and proline.

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EXCHANGE OF ISOTOPIC SULFUR BETWEEN HYDROGEN SULFIDE AND 2-MERCAPTOBENZOTHIAZOLE

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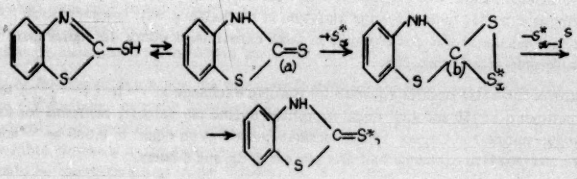
A study of the exchange reaction for elementary sulfur and the sulfur of 2-mercaptobenzothiazole [1, 2] led us to the hypothesis that this reaction proceeds only with the thiono tautomer (a) of the latter.* The mechanism for the exchange reaction can be depicted by the following scheme:



in accord with which the exchange is realized due to the reversible addition of elementary sulfur at the C=S double bond of the thiono tautomer. The addition is possible because of the ease with which the covalent bonds in multiatomic sulfur molecules become polarized.

The purpose of the present investigation was to further study the mechanism of related exchange reactions. The data on the velocity of the exchange reaction between the sulfur of Captax and the sulfur of hydrogen sulfide are of interest, first, for judging as to the mechanism of the exchange and, second, in connection with the study of the mechanism of the action of rubber vulcanization accelerators. It is known that hydrogen sulfide is formed in the vulcanization; consequently, the elucidation of the details for the whole process cannot be fully achieved without taking into consideration the reaction of both sulfur and hydrogen sulfide with Captax.

EXPERIMENTAL

The exchange reactions were run in the following manner. Hydrogen sulfide, obtained by the action of anhydrous phosphoric acid on labeled zinc sulfide, was passed into toluene, cooled with solid carbon dioxide. After warming the obtained toluene solution of hydrogen sulfide to room temperature and determining its hydrogen sulfide content (by means of standard iodine and thiosulfate solutions) the solution was poured as 9 ml aliquots into ampuls containing known amounts of 2-mercaptobenzothiazole. After being filled the ampuls were immersed in liquid air and sealed there. The apparatus shown in Fig. 1 was used to fill the ampuls. The change in hydrogen sulfide concentration in the toluene while filling the ampuls was controlled by periodic removal of samples from the solution and titrating them. With a hydrogen sulfide concentration of 0.15-0.2 mole/liter in the toluene the amount of its reduction in 9 ml of solution during the time of filling the ampuls failed to exceed 1-2 mg. The sealed ampuls were heated in a thermostat at 170, 165, 150 and 135° (± 0.2°). Under the indicated conditions the Captax dissolved completely in the toluene solution of hydrogen sulfide. On conclusion of the given time of exchange the ampuls were again cooled in liquid air, opened, and the hydrogen sulfide distilled from them into a solution of zinc acetate. The distillation was first run with warming to room temperature, and then on the boiling water bath for at least another 30 minutes after the evolution of hydrogen sulfide bubbles had ceased. The toluene solution of Captax remaining in the ampul was evaporated to dryness, after which the deposit was dissolved in 0.5% sodium hydroxide solution. The Captax was precipitated from the alkaline solution by acidification with

* The hypothesis that in solutions 2-mercaptobenzothiazole is capable of existing in two tautomeric forms, the thiono and the thiol, was recently confirmed by the spectral method and by means of dipole moment determinations [3].

hydrochloric acid. For purification of the Captax the reprecipitation was repeated at least three times. The obtained 2-mercaptobenzothiazole had m.p. 178–179°, the same as the starting compound.

The zinc sulfide, obtained from the hydrogen sulfide, and the Captax obtained after exchange, were oxidized by the Carius method. The obtained sulfate was precipitated as the benzidine salt. The activity measurements were always made on samples of the same weight (4 mg of the salt). The amounts of the taken substances, the time and temperature of heating, and also the activity of the sulfur in the starting hydrogen sulfide and in both of the reaction components, are all given in Table 1.

By means of preliminary experiments it was shown that the kinetics for the exchange of sulfur between Captax and hydrogen sulfide can only be studied at temperatures below 150°. At 175 and 165°, in parallel with the exchange reaction, there also proceeds the chemical reaction of hydrogen sulfide with Captax, during which process the hydrogen sulfide is consumed and compounds not investigated by us are formed, from which compounds the Captax could not be freed either by its repeated reprecipitation from weakly alkaline solution or by its recrystallization from organic solvents. Apparently, the above indicated chemical reaction also takes place at 150°, but only to slight degree, since the radioactive isotope balance for the experiments with a heating period of up to 10 hours agrees to within 5%. When the heating is extended to 20 hours the variation in the balance will however reach 20%. A considerable variation in the radioactive balance was also observed in those experiments where the molar ratio of Captax to hydrogen sulfide was considerably greater than one.

The application of the usual kinetics equation for isotopic exchange $kt = -\ln\left(1 - \frac{x}{x_\infty}\right)$ to the data obtained in the exchange experiments at 150 and 135° made it possible to find the velocity constants for the exchange of sulfur between hydrogen sulfide and Captax, which constants proved to be equal to 0.039 hr^{-1} and 0.117 hr^{-1} at 135 and 150°. This corresponds to exchange half-life periods of 18 and 6 hours.

TABLE 1

Exchange Experiments of 2-Mercaptobenzothiazole with Hydrogen Sulfide (Toluene as Solvent)*

Expt. No.	Time of Heating (Hrs)	Amounts of Substances Taken (in g)		Activity				Percent Exchange**	k (hr.$^{-1}$)	$\tau_{1/2}$ (hr)	Variation in the Radioactive Isotope Balance (in %)
				In starting H_2S	At Full Exchange	After Exchange					
		Captax	H_2S			In Captax	H_2S				
				Experiments at 135°							
1	3	0.3350	0.0598	3400	1590	103	3180	12	0.044		0
2	6	0.3330	0.0595	3400	1610	194	3090	29	0.038		−1.3
3	12.7	0.3325	0.0592	3610	1690	311	2850	38	0.038		−1.7
4	18.0	0.3335	0.0589	3610	1680	453	2750	49	0.037		+3.4
						Average			0.039	17.8	
				Experiments at 150°							
5	1.5	0.3325	0.0612	3610	1720	150	3360	15	0.108		+2.5
6	3	0.3325	0.0605	3610	1710	218	3120	26	0.100		0
7	6	0.3328	0.0608	3610	1710	456	2500	56	0.129		−2.6
8	10	0.3325	0.0602	3610	1700	–	2260	–	0.131		–
9	10	0.3333	0.0463	3400	1380	525	–	73	–		–
10	20	0.3330	0.0506	3400	1460	763	2000	–	–		+20
						Average			0.117	5.9	
11	3	0.3323	0.0478	3400	1410	194	3040	23	0.087		+5
12	6	0.3325	0.0475	3400	1400	300	2660	40	0.085		+4.5
						Average			0.086	8.0	

* Experiments 1-10 were run with 9 ml of solvent and Experiments 11 and 12 with 18 ml.

** Average of the data on the activities of the isolated sulfur and Captax.

It can be seen from Fig. 2 that the values of $-\ln\left(1-\frac{x}{\infty}\right)$ as a function of the time can be satisfactorily plotted on straight lines, passing through the coordinate origin. The energy of activation for the exchange, calculated by the Arrhenius equation, is equal to 25,100 cal./mole.

In studying the reaction for the exchange of sulfur between potassium xanthate and elementary sulfur, and also between sodium diethyldithiocarbamate and sulfur, it was revealed [4, 5] that the velocity constant is independent of the dilution, a situation that should not prevail in exchange by the bimolecular mechanism. This fact is of considerable interest since it is evidence that the velocity of exchange in the above mentioned cases is determined by some monomolecular stage in the transformation of one of the exchanging substances.

We postulate that only the activated diethyldithiocarbamate or xanthate molecules specifically enter into exchange reactions. In such case the speed of the whole exchange reaction will be determined by the speed of the monomolecular activation stage:

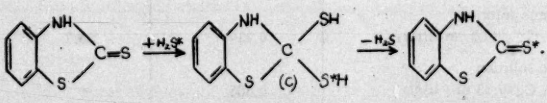
$$A \xrightarrow[\text{slow}]{} A_{\text{activated}} \xrightarrow[\text{fast}]{+S} \text{Intermediate compound of type (b).}$$

However, when exchange in the system Captax-sulfur was studied it was found that when the reaction was run in dilute solutions, with former molar ratios of starting substances kept constant, that a reduction in the velocity constants of the exchange, calculated by the above presented equation [6, 7] was observed.

It was also of interest to determine the relationship existing between the concentration and the apparent velocity constants for the exchange of sulfur between Captax and hydrogen sulfide. For this purpose the amount of solvent for the previously used weights of exchanging substances was doubled. From Fig. 2 it can be seen that dilution results in considerable decrease in the velocity constants. In dilute solutions $\underline{k} = 0.086$ hr.$^{-1}$ instead of 0.117 hr.$^{-1}$ (at 150°). It should be mentioned that in the dilution the total concentration of the Captax and hydrogen sulfide is reduced by a factor of 2.2. However, this led to a reduction of only 1.4 times in the velocity constant. Such a divergence exceeds the possible experimental errors and testifies to the fact that the reaction for the exchange of sulfur between Captax and hydrogen sulfide fails to be strictly bimolecular in nature. The absence of proportionality between the total concentration of reacting substances and the exchange velocity constants is also observed for the exchange of Captax with elementary sulfur [6, 7] and has, apparently, general reasons.* These data testify to the fact that the speeds of the exchange reactions for both sulfur and hydrogen sulfide are no longer determined by the speed of the monomolecular activation stage. At the same time these reactions also fail to proceed by the normal bimolecular mechanism. It can be assumed that in these systems the transformation rate of Captax into the activated state and the reaction rate of the latter with sulfur (or hydrogen sulfide) are commensurate:

$$A \xrightarrow[\text{slow}]{} A_{\text{activated}} \xrightarrow[\text{slow}]{+S} \text{Intermediate compound of type (b).}$$

We postulate that the exchange reactions of Captax with both sulfur and hydrogen sulfide proceed by one and the same mechanism. In these reactions there occurs heterolytic cleavage of the C – S bond with the formation of the corresponding intermediate compounds. In the case of exchange with hydrogen sulfide such a compound should be represented by (c):



A similar reaction mechanism was evaluated for the exchange of oxygen between aldehydes or ketones and water [8], and also between inorganic acids and water [9].

* On the basis of the data obtained in her study [7] E. N. Guryanova concludes that the apparent exchange velocity constant depends only on the concentration of the Captax and is independent of the sulfur concentration. A considered evaluation of the data presented in the indicated study [7], and of the results obtained by us [6], shows that this statement is without sufficient basis and that the apparent velocity constants for the reaction actually depend on the concentrations of both of the reaction components.

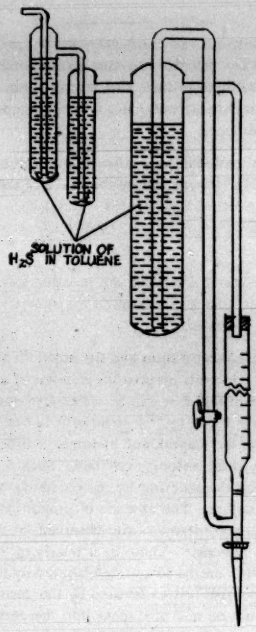


Fig. 1. Apparatus for ampul filling.

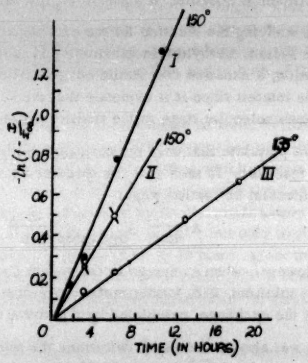


Fig. 2. Variation in the values of $-\ln(1-\frac{x}{x_\infty})$ with time (from the data of Table 1). I) Experiments 5-10, II) Experiments 11-12, III) Experiments 1-4.

In conclusion it is interesting to compare the results of this study with the data on the kinetics of sulfur exchange between Captax and elementary sulfur, which data are given in Table 2.

The data given in Table 2 show that the exchange reactions with both sulfur and with hydrogen sulfide possess extremely close kinetic characteristics.

TABLE 2

Velocity Constants for Exchange at 150° and the Energy of Activation of the Exchange Reactions

Exchange in the System	k (hr^{-1})	E (k cal / mole)	Literature Reference
Captax-H_2S^* in toluene solution (C_k=0.22 m., C_{H_2S}=0.2 m/liter)	0.117	25.1	our data
Captax-S^* in toluene solution (C_k=0.33 m., C_S=0.33 m / liter)	0.365	—	[6]
Captax-S^* in napthalene solution (C_k=0.24 m/ liter)	0.576	24.0	[7]

SUMMARY

1. The method was proposed for studying the exchange reactions between the sulfur of hydrogen sulfide and the sulfur contained in organic compounds.

2. The kinetics for the exchange reaction of sulfur in the system 2-mercaptobenzothiazole-hydrogen sulfide was studied and it was shown that this exchange reaction has a fractional order.

3. The possible mechanism of exchange reactions with hydrogen sulfide participation was examined.

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